THE THERMALLY REVERSIBLE NATURE OF THE
AROMATIC URETHANE BOND

By

MARK ALLEN MURLA

Dedicated to Joseph and Wilma Murla.

All they ever asked was for me to be the best I could be.

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In the end, it seems as if the actual experimental work is only a small part of what it takes to obtain a PhD. So many other things are necessary, and the help of so many people becomes indispensable. I would like to thank all of my family, especially my sister, Pamela. She has kept me straight for many years. I also want to thank Steven Thompson who has been a long distance pair of hands during this last year.

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As polymers gain increasing uses as replacement materials for metals,
glass and paper, the need for reusable and recyclable plastics has become more
desirable. Today, polyurethanes have become an important class of polymeric
materials. The urethane bond could serve as a thermally reversible link in
polymers since urethane compounds are formed via an adduct forming reaction;
there is no loss of an atom or molecule. These adduct forming reactions could
provide the mechanism for recyclable polymers.

In order to evaluate the reversible nature of the urethane bond, a novel
polyurethane system was synthesized in addition to model compounds. This
polymer was designed such that the only bond capable of thermally reversing
was the urethane bond, and the polymer was prepared via the chain extension of
a low molecular weight oligomer of polyoxyethylene. The monomers were
synthesized by directly functionalizing an oligomer of polyoxyethylene with
aromatic functional groups, and these compounds were converted to α,ω-
isocyanatobenzene terminated and α,ω-phenol terminated polyoxyethylene
prepolymers.

The thermally reversible properties of the model and polymeric urethanes were characterized using differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and hot-stage infrared spectroscopy (HS-IR). These techniques were used to examine the thermal reversibility of the urethane bond in the bulk state. Both the nature of the substituent and the physical state of the material affected dissociation. Electron-withdrawing groups on the phenol and electron-releasing groups on the isocyanate favored dissociation as compared to an unsubstituted aromatic-aromatic urethane bond.

The physical state of the material was observed to have an effect upon dissociation, and no dissociation occurred until the urethane compounds had melted. When the urethanes were studied in a solvent, the dissociation occurred at lower temperatures than in the bulk state. In the absence of solvent, upon melting, the presence of isocyanate was observed in the infrared spectrum; and the strength of the absorption increased as the temperature was increased. The reversible reaction was observed to occur in the absence of solvent in that the isocyanate absorption decreased upon cooling.

CHAPTER 1
INTRODUCTION

In today's applications of polymers, there is an increasing demand for materials that exhibit special characteristics; one such characteristic is the ability to produce a polymer composition that is reusable. The need for finding plastics capable of being recycled for other applications becomes of increasing importance as they find greater uses as replacement materials for metals, glass and paper. An additional advantage is the ability to completely recycle the substance via depolymerization to monomer that can be reused to form a new polymer.

With these targets in mind, one objective of this research has been to synthesize model aromatic urethanes and characterize their thermally reversible behavior. Another objective has been to predict the utility of such a functionality as a thermally reversible covalent link in polymers. Polyurethanes are generally formed under bulk polymerization conditions, i.e. in the absence of solvent. In the applications of polyurethanes, the polymer is generally exposed to heat in the absence of any solvent; therefore, the thermally reversible properties of the urethane bond have been studied under bulk conditions.

In order to maintain an entirely reversible system, a closed system must exist. Two examples of a closed system are either one in which all reactants, products and catalysts are contained within the system and a second employing adduct forming reactions. The first case is often difficult to achieve due to the loss of small molecules because of their volatility or extraction during applications of the polymers. The latter example is more feasible and can be achieved in chain

$$\text{R-NCO} + \text{HO-R'} \xrightarrow{\hspace{2cm}} \text{R-NHCO}_2\text{-R'}$$

Figure 1-1. An adduct forming urethane reaction.

extension polymerizations using a step polymerization, addition type mechanism. The formation of the urethane occurs via adduct formation in the reaction of an isocyanate with a hydroxyl containing substrate; there is no loss of any atom or molecule, and the reaction can occur without the addition of a catalyst, Figure 1-1. This adduct forming reaction suggests the possibility of its use in a chain extension polymerization to create a polymer capable of reversing thermally ; a generalized example of this is shown in Figure 1-2. If one chooses the "A" functionality to be an isocyanate group and the "B" functionality to be a hydroxyl group, a reversible polyurethane system can be produced. The urethane bond could serve as a thermally reversible covalent link in a linear chain extended polymer or as a thermally reversible covalent crosslink in a network polymer.

$$n\,\text{A}\!-\!\!-\!\text{A} + n\,\text{B}\!-\!\!-\!\text{B} \xrightarrow{\hspace{2cm}} \text{-(-A}\!-\!\!-\!\text{A-B}\!-\!\!-\!\text{B-)}_x\text{-}$$

$$n\,\text{OCN}\!-\!\!-\!\text{NCO} + n\,\text{HO}\!-\!\!-\!\text{OH} \xrightarrow{\hspace{1.5cm}} \text{-(-CONH}\!-\!\!-\!\text{NHCO}_2\!-\!\!-\!\text{O-)}_x\text{-}$$

Figure 1-2. A thermally reversible polymer system.

The urethane bond has become an important chemical structure in polymer chemistry today, and large quantities of polyurethanes are produced each year. While this is the case, the investigation and characterization of new

polyurethanes has not been pursued in more recent years. Therefore, the thermally reversible nature of the urethane bond has been investigated here in an effort to predict the design of a thermally reversible polymer. In such a system, the molecular weight of the polyurethane would be a function of temperature. When this type of polymer is heated above the temperature at which reversible dissociation begins, the molecular weight would decrease; and conversely, as the temperature decreases, the molecular weight would then increase. Due to the importance of the urethane link in polymer chemistry, the investigation of the thermally reversible properties of the urethane bond is useful in evaluating its applications as a thermally reversible covalent link.

Chemistry of Urethane Formation

The first urethane of any kind was synthesized in 1849 by Wurtz[1] from the reaction of ethyl isocyanate (1) with ethanol (2) to form N-ethyl ethyl carbamate (3), Figure 1-3. This type of urethane bond is an aliphatic-aliphatic urethane bond since it results from the reaction of an aliphatic isocyanate with an aliphatic alcohol, and also this is an addition reaction since all the atoms required for the formation of the urethane functional group are present in the isocyanate and hydroxyl precursors, (1) and (2). The first fully aromatic isocyanate, phenyl isocyanate, was prepared in 1850 by Hofmann.[2] The synthesis of this new class of isocyanates provided new possibilities for other types of urethanes. The type of bond formed by the reaction of an aromatic isocyanate, such as phenyl

$$CH_3CH_2\text{-}NCO \ + \ HO\text{-}CH_2CH_3 \ \longrightarrow \ CH_3CH_2NHCO_2CH_2CH_3$$

(1) (2) (3)

Figure 1-3. First formation of an aliphatic-aliphatic urethane bond.

Figure 1-4. Formation of an aromatic-aromatic urethane bond.

isocyanate (4), with an aromatic hydroxyl compound, such as phenol (5), Figure 1-4, is an aromatic-aromatic urethane bond, N-phenyl phenyl carbamate (6), since both precursors are aromatic compounds.

In fact, four classes of urethane compounds exist, dependent upon the nature of the isocyanate and the alcohol used in forming them, Table 1-1. Each class exhibits different thermal behavior, according to the stability of the urethane, as well as the reactivity of the isocyanate and hydroxyl functional groups. The reaction of an aliphatic alcohol with an aliphatic isocyanate proceeds at low temperatures without the necessity of an added catalyst, since alcohols are sufficiently nucleophilic to attack the isocyanate functional group, Figure 1-5.[3] An examination of the resonance structures for the isocyanate group in Figure 1-6 shows the propensity of this functionality to undergo nucleophilic attack by alcohols; there is a positive charge located at the carbon atom of the isocyanate.

Table 1-1. Four Classes of Urethane Bonds.

Nature of Reactants	Class of Urethane
Aliphatic isocyanate with aliphatic alcohol	Aliphatic-Aliphatic urethane
Aliphatic isocyanate with aromatic phenol	Aliphatic-Aromatic urethane
Aromatic isocyanate with aliphatic alcohol	Aromatic-Aliphatic urethane
Aromatic isocyanate with aromatic phenol	Aromatic-Aromatic urethane

$$R-N=C=O \ + \ HO-R' \longrightarrow \overset{\overset{-O \ H}{|\ |}}{\underset{+}{R-N=C-O-R'}}$$

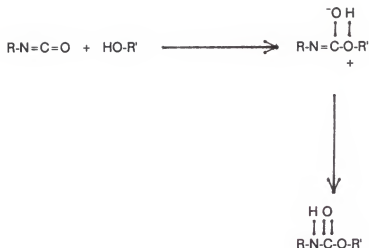$$\overset{\overset{H \ O}{|\ |}}{R-N-C-O-R'}$$

Figure 1-5. Nucleophilic attack of the oxygen towards an isocyanate.

These resonance structures suggest that an aromatic isocyanate would be more reactive towards both aliphatic and aromatic alcohols since an aromatic ring is not as electron-releasing as an alkyl group. Reaction of an aromatic or aliphatic isocyanate with an aliphatic alcohol proceeds readily at low temperatures.

$$\overset{-\ +}{R-N-C=O} \longleftrightarrow R-N=C=O \longleftrightarrow \overset{+\ -}{R-N=C-O}$$
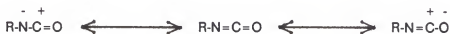
Figure 1-6. Resonance structures of the isocyanate group.

The situation differs for phenols, however, since they are less nucleophilic. Thus, the low temperature reaction of an aromatic phenol with either an aliphatic or aromatic isocyanate requires a catalyst such as a tertiary amine or organometallic compound.[3-6] In a series of urethane compounds studied under identical conditions, the following observations may be made based on relative reactivity. A urethane made from an aliphatic alcohol and an aliphatic isocyanate

should show a lesser tendency to reverse than that from an aliphatic alcohol and an aromatic isocyanate. Similarly, a urethane from a phenol and an aromatic isocyanate should show a greater tendency to reverse than that from a phenol and an aliphatic isocyanate.

The reversible nature of the urethane bond may not be dependent solely upon the reactivities of the precursors; other factors can affect dissociation such as substituents, physical state, solvent effects and concentration. These additional factors may lead to different dissociation properties in the pure state as compared to the dissolved state, and some of these factors have been studied in this research.

<u>Background of the Dissociation of Model Urethane Compounds</u>

The first investigation of the thermal dissociation of an aromatic-aromatic urethane bond was performed as early as 1890 by R. Leuckart,[7] where the dissociation of the aromatic-aromatic urethane, N-phenyl phenyl carbamate (<u>6</u>), to phenol (<u>5</u>) and phenyl isocyanate (<u>4</u>) was studied as a suspension of the urethane in mineral oil, Figure 1-7. During heating, dissociation was observed by measuring the appearance of the isocyanate stretching absorption in the infrared spectrum; and at the time, the specifics of the dissociation were not fully investigated. More importantly, the thermally reversible nature of the urethane bond was not recognized for its potential.

Figure 1-7. Decomposition of an aromatic-aromatic urethane, phenyl carbanilate.

More than 60 years later, the dissociation characteristics of the urethane bond were investigated more thoroughly. In 1952, a series of mechanistic studies of urethanes in solution was done by Hoshino, Mukaiyama and others[8-25]; and their work did much to elucidate the mechanism and conditions under which dissociation occurred in various solvents. Indirectly, they examined the reversible nature of the aromatic-aromatic urethane bond by in-situ trapping the formed isocyanate with various highly reactive trapping agents such as butyric acid, Figure 1-8.[8] A mechanism for the decomposition of a urethane in butyric acid was suggested where the first step was the dissociation of N-phenyl phenyl carbamate (6) to phenyl isocyanate (4) and phenol (5). The isocyanate would then react with butyric acid to form a new adduct product (7) that under the conditions referenced would undergo decarboxylation to produce carbon dioxide and N-phenyl butyramide (8). Meanwhile, the phenol formed in the first step would also react with butyric acid to produce phenyl butyrate (9). In these trapping experiments, rates of decomposition of the carbamate (6) were measured by monitoring the rate of carbon dioxide evolution from the reaction of the presumed phenyl isocyanate with the protic acid solvent. No evidence of carbon dioxide evolution was observed at refluxing acetic acid temperatures of 118°C; however, carbon dioxide was evolved in butyric acid above 130°C. Since no carbon dioxide was evolved at 118°C, it was concluded that no dissociation had occurred; however, this presumes that step one or two is rate determining for the decomposition reaction. If the new adduct (7) does not undergo decarboxylation at 118°C, this does not mean that no dissociation occurred. It merely suggests that temperatures of 130°C were required for the decarboxylation of the new adduct (7). Nonetheless, Hoshino et al.[14-16] proposed a mechanism for the
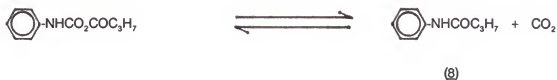
Figure 1-8. Trapping experiments in the dissociation of aromatic urethanes.

thermally reversible urethane reaction from a series of these experiments involving urethanes as well as urea compounds, Figure 1-9.

In the first step of this mechanism, a tautomerization occurs in which electron density shifts towards the formation of an O-H bond, (<u>6</u>) to (<u>10</u>). This tautomer (<u>10</u>) then undergoes a proton transfer to produce the charge separated species (<u>11</u>) in the second step; this step has been shown to occur via an intramolecular transfer using isotopic labeling studies. The charge separated
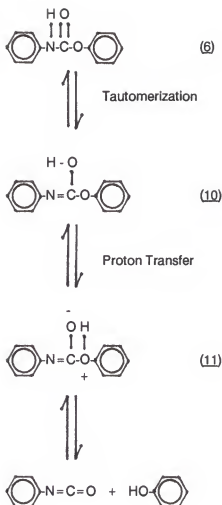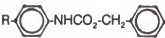
Figure 1-9. Proposed mechanism for the reversible dissociation of aromatic urethanes.

species then readily delocalizes the separated charges enabling dissociation to the isocyanate and phenol.

In 1957, Mukaiyama and Iwanami[10] continued the investigation of the thermal dissociation of urethanes by measuring the rates of dissociation of a series of substituted carbamates in a solvent mixture of ethanolamine and benzyl alcohol, where the substituent was present only on the "isocyanate portion" of the
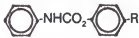
Table 1-2. Substituent Effects on the Isocyanate.

$$R-\langle\bigcirc\rangle-NHCO_2-CH_2-\langle\bigcirc\rangle$$

	R	mp ($^\circ$C)
(12)	H	78
(13)	p-CH$_3$O	99
(14)	p-NO$_2$	155

urethane, Table 1-2. In this series, the presence of the nitro group was found to favor dissociation, and the rate was observed to increase with the introduction of the nitro group as a result of a lower energy of activation for dissociation. The electron-withdrawing nature of the para-nitro group assisted in weakening the N-H bond thereby increasing the acidity of the urethane hydrogen; therefore, donation of the proton to a basic solvent was facilitated. This was contrary to resonance considerations where an electron-withdrawing group would increase the electrophilic character of the isocyanate group; therefore, dissociation should be disfavored.

Later, in 1960 Mukaiyama et al.[11] continued with another series of urethanes where the substituent was present only on the "alcohol side" of the urethane, Table 1-3. In this study, the effect of substituents on the phenol portion was evaluated; and it was found that electron-withdrawing groups again increased the rate of dissociation in the presence of amines by lowering the energy of activation. An explanation for a basic solvent favoring dissociation for the para-nitro group was that due to the greater acidity of p-nitrophenol, upon dissociation, the p-nitrophenol would react to a greater extent than

Table 1-3. Substituent Effects on the Alcohol.

	R	mp (°C)
(6)	H	126
(15)	p-CH₃O	133
(16)	p-NO₂	145-146

p-methoxyphenol in an acid-base equilibrium, Figure 1-10. The more electron-withdrawing group shifts the equilibrium towards the right.

Figure 1-10. Acid-base equilibrium of the formed p-nitrophenol.

In 1971, Lateef et al.[26] conducted a similar study of the thermal dissociation nature of the urethane bond. Once again this study of the aromatic-aromatic urethanes was done in solution; however, glyme was used as the solvent since this solvent was non-reactive towards the dissociation products. The same group of compounds in Table 1-3 were studied wherein the equilibrium concentrations of the urethane and the isocyanate formed during the dissociation in glyme were measured. Unlike the previous kinetic experiments conducted by Mukaiyama, Lateef et al. used infrared spectroscopy to actually measure the presence of isocyanate formed from the dissociation; however, Lateef et al. still did not determine if the reaction could be considered completely reversible. In these experiments, it was found that equilibrium was reached within 2 minutes at a

temperature of 150°C. However, no cooling experiments were conducted to determine whether competing reactions would prevent the system from being completely reversible.

These dissociation studies have shown that model urethane compounds are capable of thermally dissociating when heated in solvents of either a participating or a non-participating nature. The temperatures at which dissociation occurs in solution and the equilibrium nature have been measured. However, the studies were not conducted in the bulk state that would be encountered in applications, and it was unlikely that the urethane bond would exhibit the same behavior under these conditions.

Background of the Dissociation of Polyurethanes

While the reversible nature of model urethane compounds has been examined; and although polyurethanes have been known since Otto Bayer first synthesized them in 1937,[27-32] it was not until the 1970s that the reversible nature of the urethane bond in a polymer was reported. This observation actually was accidental, and since that time there has been very little systematic work to examine the reversible nature of polyurethanes. One of the first examples was reported in a paper by Kinstle and Sepulveda[33]; a "sublimeable" polymer was observed during the thermal characterization of poly(oxycarbonylimino-1,4-phenylene) (17), that contains only aromatic-aromatic urethane bonds.

$$-(-O-\langle\bigcirc\rangle-NHCO-)_n-$$
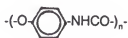
(17)

Differential scanning calorimetry (DSC) measurements on the polymer (17) showed no melting behavior, while thermogravimetric analysis (TGA) showed a substantial weight loss at 200°C under vacuum. During the thermolysis of (17), condensation of a solid material was observed on the cooler surfaces of the thermolysis tube; and analysis of this condensed material by spectroscopy supported the structure of the original polymer. Kinstle and Sepulveda explained these results through a thermal decomposition of the polymer (17) to monomer, p-hydroxyphenyl isocyanate (18), which then re-polymerized upon cooling, Figure 1-11.
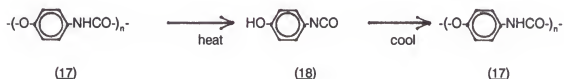

-(-O-⟨◯⟩-NHCO-)$_n$- $\xrightarrow{\text{heat}}$ HO-⟨◯⟩-NCO $\xrightarrow{\text{cool}}$ -(-O-⟨◯⟩-NHCO-)$_n$-

(17)   (18)   (17)

Figure 1-11. Thermolysis of poly(oxycarbonylimino-1,4-phenylene).

As recent as 1980, some researchers still felt that the reaction of an isocyanate with an alcohol was irreversible. Orzeszko and Kolbreck[34] studied a model urethane (19) and a phenyl isocyanate capped polyoxyethylene (20) for dissociation properties. The model (19) had a melting point of 155°C, and thermogravimetric analyses of both (19) and (20) showed weight loss decompositions above 230°C. Additionally, pyrolysis studies conducted between 230 and 300°C did not show evidence of phenyl isocyanate nor ethylene glycol. Ballistreri et al. viewed these results to be in conflict with earlier work that showed the urethane bond to be capable of dissociation to isocyanate and alcohol.[35-47] Ballistreri et al.[47] explained that the absence of isocyanate and ethylene glycol did

not disprove dissociation; at the pyrolysis temperatures used, they suggested that water produced from the decomposition of ethylene glycol would react with phenyl isocyanate to produce aniline and carbon dioxide.

(19)   (20)
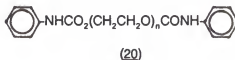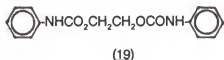
Another prepolymeric model was studied by Bill et al.[48] This prepolymer was a phenyl isocyanate endcapped α-hydro-ω-hydroxy-oligo(oxytetramethylene) (21). These prepolymers were studied by differential scanning calorimetry and showed melting points from 47 to 180°C, but no evidence of dissociation was reported.

n = 1-6
(21)
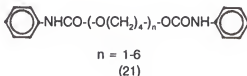
In 1981, another polyurethane system was examined for thermal dissociation properties. As with the model urethanes, these studies were performed in solution. Kawakami et al.[49] synthesized a polymer (22) of the repeating structural unit found in Figure 1-12. Thermal dissociation experiments were done as dilute solutions of the polyurethane in diglyme, and an increase in isocyanate formed by the dissociation of (22) in diglyme was observed as the temperature was raised from 110°C to 150°C. Kawakami et al. measured only the change in the intensity of the NCO stretching absorption in the infrared spectrum, stating it was difficult to follow the change in the urethane C=O intensity. This difficulty might be explained by an examination of the micro-structure of the
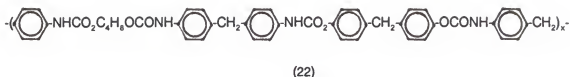
(22)

Figure 1-12. Structure of the aromatic polyurethane synthesized by Kawakami.

polymer repeat unit in Figure 1-12. The polymer (22) contains two types of urethane bonds, an aromatic-aromatic type and an aromatic-aliphatic type, the latter from a substituted aromatic isocyanate and aliphatic alcohol. At elevated temperatures, both types of bonds could dissociate. Initially as the polymer (22) is heated, the more thermally labile aromatic-aromatic urethane bond would begin to dissociate, predicted from resonance considerations. As the temperature is raised, the extent of dissociation would increase; however, the aromatic-aliphatic urethane bond would also begin to dissociate. In an effort to determine which type of bond dissociated, Kawakami attempted to measure the thermal dissociation of the two model urethanes shown below which contain an aromatic-aliphatic urethane bond, N-phenyl ethyl carbamate (23) and N-phenyl n-butyl carbamate (24), Figure 1-13. No detectable dissociation was observed in either case; however, neither model, (23) nor (24), contains electron-releasing substituents in the para position of the aromatic ring. From earlier discussions, electron-releasing groups reduce the electrophilicity of the isocyanate and should favor dissociation. In the polymer (22), the aromatic-aliphatic urethane bond is para substituted with an electron-releasing group, and this group reduces the reactivity of an isocyanate towards nucleophiles and favors the presence of isocyanate in the equilibrium.

CH₃CH₂OCONH- ⬡   and   CH₃CH₂CH₂CH₂OCONH- ⬡
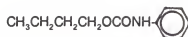
(23)   (24)

Figure 1-13. Urethane models used by Kawakami.

More recent studies of the thermal properties of polyurethanes have focused on the physical changes that occur upon heating. Coleman et al.[50] studied the changes in hydrogen bonding of poly(1,4-butylene hexamethylene carbamate) (25) as a function of temperature. This polymer had a melting point of 182°C; but upon heating to a temperature of 210°C, no evidence of dissociation was observed in the infrared spectrum.

⬡-(-CONH(CH₂)₆NHCO₂(CH₂)₄O-)ₙ-⬡

(25)

Lee et al.[51] studied a block copolymer of poly(propylene oxide) and poly(butanediol bis(methylene diisocyanate)) (26) for phase separation as a function of temperature. The polymer had a melting point of 100°C, but no dissociation was reported at a temperature of 110°C.

-(-CH₂CH(CH₃)-O-)₃₄-(-CONH-⬡-CH₂-⬡-NHCO₂(CH₂)₄O-)ₙ-

(26)

While these experiments have shown that the urethane bond in some polymers can undergo thermal dissociation, none of these experiments

demonstrates that a completely reversible polyurethane exists. Many of the studies have focused on polymers with an aromatic-aliphatic urethane bond which should behave differently than an aromatic-aromatic urethane bond.

The Challenges of a Thermally Reversible System

A prediction of reactivity based upon structure predicts that of the four classes of urethanes, the aromatic-aromatic type has the best chance to show thermal reversibility. In order to fully delineate the requirements for a thermally reversible urethane link in a polymer, a systematic analysis of the aromatic-aromatic urethane bond has been undertaken in this dissertation to predict its utility in a thermally reversible system. The aromatic-aromatic urethane bond has been evaluated under the physical conditions encountered during many polyurethane syntheses and applications, most notably bulk conditions.

In this research, the effect of chemical structure has been evaluated first by studying a series of model aromatic-aromatic urethanes. This series demonstrated the effects of electron-withdrawing and electron-releasing substituents upon the thermally reversible nature of the urethane bond in a bulk state. The model urethanes in Table 1-4 have been examined.

A polymer system appropriate for developing a thermally reversible polyurethane should not contain any other bonds that may be thermally labile. A polyether-based polyurethane was chosen as the system to be studied since the polyether backbone is thermally stable and allows characterization of the reversibility of the urethane bonds without interference. The conventional method of synthesizing a polyether-based aromatic urethane is outlined in Figure 1-14, where the polyether ($\underline{33}$) is first reacted with an aromatic diisocyanate such as methylene bis-phenyl isocyanate ($\underline{34}$) to generate an α,ω-isocyanate terminated

Table 1-4. Model Aromatic-Aromatic Urethanes Studied.

$$R\text{-}\langle\bigcirc\rangle\text{-}NHCO_2\text{-}\langle\bigcirc\rangle\text{-}R'$$

	R	R'
(6)	H	H
(27)	NO_2	H
(28)	CH_3O	H
(16)	H	NO_2
(29)	NO_2	NO_2
(30)	CH_3O	NO_2
(15)	H	CH_3O
(31)	NO_2	CH_3O
(32)	CH_3O	CH_3O

polyether prepolymer (35). It is considerably easier to synthesize a new isocyanate prepolymer by this method than to directly functionalize the polyether with an aromatic group. The prepolymer (35) then is used in a chain extension polymerization by the reaction with either a bis-hydroxyl compound (36) or bis-amino compound to produce a polyurethane (37) or a polyurethane/urea. A considerable disadvantage in the approach in Figure 1-14 is the incorporation of an aliphatic-aromatic urethane bond into the polymer (37). A polyurethane formed via the conventional synthetic route would contain a mixture of different urethane bonds, and as has already been shown all types of urethane bonds are capable of dissociating. As was seen in the polymer system (22) of Kawakami et al.,[49] the presence of more than one type of urethane bond can cause difficulties in characterization. A polymer containing several types of urethane bonds may not form a reversible system. If upon heating, the several types of bonds dissociate, then the polymer could repolymerize with scrambling. The reformed
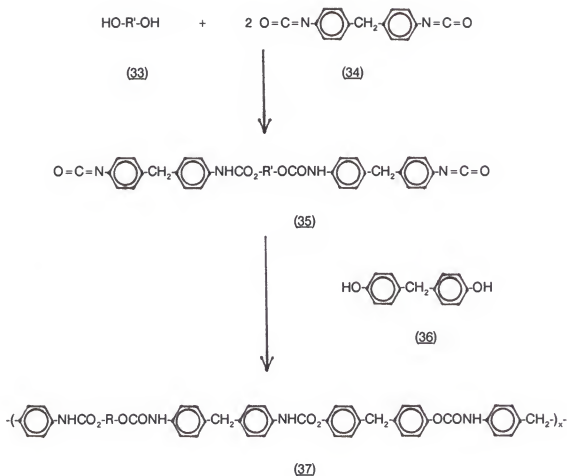
Figure 1-14. Chain extension using isocyanates to form polyurethanes.

polymer would be structurally different and most likely exhibit different physical properties as compared to the original material. Thus, this approach (Figure 1-14) was not taken.

A goal of this research has been the synthesis of a new polyether-based polyurethane containing only urethane bonds of the aromatic-aromatic type, thereby eliminating the incorporation of an urethane bond of the aromatic-aliphatic type. Such a polymer would not suffer scrambling during reversible dissociation. Low molecular weight oligomers of poly(oxyethylene) have been

directly functionalized to generate bis-phenol and bis-aromatic isocyanate prepolymers without incorporating a thermally labile aliphatic-aromatic urethane bond. These prepolymers have been chain extended in a step propagation, addition type polymerization to produce a polyurethane.

The synthesis of a useful polyurethane for the reversible system is achieved through the series of functional group conversions shown in Figure 1-15. In the first step, triethylene glycol (38) is directly functionalized with p-fluoronitrobenzene (39). The nitro groups in (40) are then reduced to amino groups, and the amine group (41) serves as the precursor to both the desired isocyanate (42) and the phenol (43). These prepolymers then can be used in a chain extension polymerization to produce a poly(oxyethylene-urethane) (44) containing only aromatic-aromatic urethane bonds as thermally labile links.

In addition to the synthesis of the poly(oxyethylene-urethane), an objective of the research has been to characterize the thermal dissociation properties of the urethane bond. Several techniques have been chosen to characterize the thermal properties of the aromatic-aromatic urethane bond, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and hot-stage infrared spectroscopy (HS-IR), techniques which permit the direct examination of the link in the pure state. The above three techniques have been used to investigate the temperature at which dissociation begins as well as the extent of dissociation as a function of temperature in the bulk state.
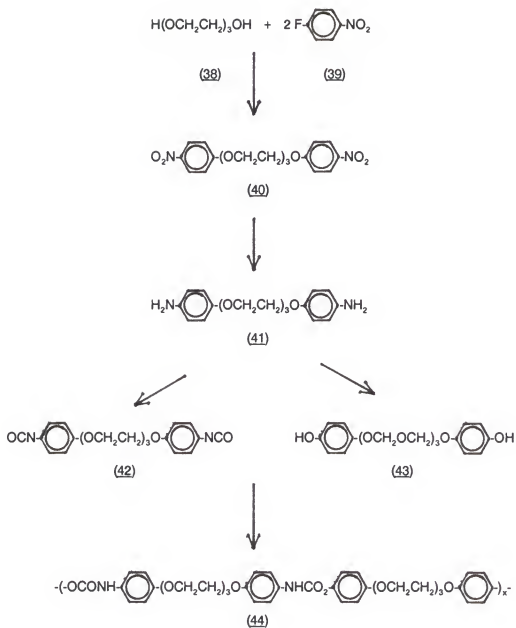
Figure 1-15. Proposed synthesis of chain extended polyoxyethlenes via the aromatic-aromatic urethane bond.

General Information

All NMR spectra were obtained from a Varian EM360L 60 MHz Spectrometer, a Varian XL-200 NMR Spectrometer or a Bruker WP-80-CW 80 MHz NMR Spectrometer. The chemical shifts are given in parts per million (ppm) downfield from the reference shift of tetramethylsilane (TMS). In some cases, the shifts were calibrated using a signal characteristic of the deuterated solvent used. The multiplicity of a resonance signal is designated as singlet (s), doublet (d), doublet of a doublet (dd), quartet (q) or multiplet (m).

Qualitative infrared spectra were obtained from a Perkin-Elmer 281 Spectrophotometer. Absorbances and percent transmittances are expressed in wavenumbers (cm^{-1}). Absorption bands are designated as weak (w), medium (m), strong (s), broad (br) and shoulder (sh).

Melting points, given in degrees Celsius, were obtained from a Thomas Hoover Capillary Melting Point Apparatus, a Fisher Johns Melting Point Apparatus or from a Perkin-Elmer Differential Scanning Calorimeter Model DSC-7 calibrated using a pure indium metal reference standard.

Elemental analyses were performed by Atlantic Microlabs Inc in Norcross, Georgia.

Gas chromatographic analyses were performed on a Hewlett Packard 5880A Series Gas Chromatograph.

Reagents were obtained from Aldrich Chemical Co., Eastman Kodak Co., Fisher Scientific and Mallinckrodt Inc unless otherwise noted. Solvents used were of reagent grade or ACS grade quality and used without further purification unless otherwise noted. Some of the solvents were purified and dried according to procedures reported in the literature.[52] N,N-dimethylformamide (DMF) was purified by mixing with potassium hydroxide pellets and distilling from either calcium oxide or barium oxide at reduced pressure. Purified chloroform was obtained by washing with concentrated sulfuric acid and water, followed by distillation from phosphorous pentoxide. The purified chloroform was stored in dark containers under a nitrogen atmosphere. Toluene was dried by distilling from sodium. Pyridine and triethylamine were dried by distilling from calcium hydride under a nitrogen atmosphere. The glyme solvents and 1,4-dioxane were dried by distilling from sodium metal several times under a dry atmosphere. Phenol was purified by sublimating at reduced pressure. Phenyl isocyanate was purified by vacuum distillation.

Syntheses of Model Compounds and Model Urethanes

(2-Methoxyethoxy)benzene[53] (45)

Into a 500 ml round bottom flask equipped with a Teflon magnetic stir bar were placed 250 ml of DMSO and 81.363 g (1.450 mol) of potassium hydroxide pellets. The mixture was stirred for about five minutes. To this mixture was then added 50.093 g (0.3630 mol) of 2-phenoxyethanol immediately followed by 102.366 g (0.7214 mol) of methyl iodide. The reaction was very exothermic. The mixture was stirred at room temperature for 24 hours. The yellowish mixture was poured into 300 ml of water. The basic solution was then extracted with

methylene chloride (4 x 200 ml). The organic layer was washed with water (3 x 100 ml) and dried overnight with $MgSO_4$. The methylene chloride solution was filtered and then rotary evaporated to yield a slightly yellow liquid. Yield was 54.787 g (99%).

IR (Neat): 2940(s), 1604(s), 1500(s), 1250(s)

^{1}H NMR ($CDCl_3$, TMS): 3.40 (s, 3H), 3.72 (dd, 2H), 4.17 (dd, 2H) and 7.15 (m, 5H)

^{13}C NMR ($CDCl_3$, TMS): 158.24, 128.74, 120.10, 113.90, 70.27, 66.42, 58.10

Analysis for $C_9H_{12}O_2$ calculated (exp.): C,71.05 (69.32); H, 7.89 (7.83)

4-(2-Methoxyethoxy)nitrobenzene[54] (46)

To a 1000 ml 3-neck round bottom flask equipped with a thermometer, addition funnel and overhead mechanical stirrer were placed 200 ml of concentrated sulfuric acid, 200 ml concentrated nitric acid and 100 ml of water. The acid solution was cooled below 5°C. Then 18.216 g (0.2640 mol) of sodium nitrite was added. At this point, the solution became golden yellow. The addition funnel was filled with 40.014 g (0.2633 mol) of 2-methoxyethoxybenzene (45), and the aromatic ether was slowly dripped into the nitrating acid solution over a period of 1.5 hours maintaining a temperature below 5°C. The solution was stirred for a few hours below 5°C. The deep purple solution was then poured onto 1400 g of ice. A deep purple solid was suction filtered and washed with water. As the solid was washed and dried it developed an orange color. The product was recrystallized from 95% ethanol to yield orange needles. The solid had a melting point of 89-90°C. Yield was 29.414 g (57%).

IR (KBr): 3100(w), 2930(m), 1595(s), 1508(s), 1335(s), 1265(s)

IR (Deposited film from chloroform): 3100(w), 2950(m), 1595(s), 1508(s), 1335(s), 1265(s)

^{1}H NMR (CDCl$_3$, TMS): 3.48 (s, 3H), 3.77 (dd, 2H), 4.20 (dd, 2H), 6.96 (d, 2H), 8.17 (d, 2H)

^{13}C NMR (CDCl$_3$, TMS): 163.89, 141.65, 125.86, 114.61, 70.64, 68.14, 59.27

Analysis for $C_9H_{11}NO_4$ calculated (exp): C, 54.82 (54.90); H, 5.58 (5.61); N, 7.11 (7.08)

4-(2-methoxethoxy)aniline[55] (47)

To a 250 ml 3-neck round bottom flask equipped with a magnetic stir bar and condenser were placed 10.0290 g (50.91 mmol) of 4-(2-methoxyethoxy) nitrobenzene (46) in 100 ml of methanol. The solution was stirred at room temperature under nitrogen. Then 0.4289 g of 5% palladium on charcoal was added. To this stirred mixture was then added 22 g (508 mmol) of dried ammonium formate. The reaction was stirred for several hours at room temperature. An aliquot was taken and showed only about 5% reduction had taken place at this time. The mixture was then heated to 50°C overnight. The next day, a ^{1}H NMR spectrum of an aliquot showed no remaining 4-(2-methoxyethoxy)nitrobenzene. The reaction mixture was suction filtered through a pad of Celite 545. The methanol was rotary evaporated to leave a dark brown oil and some crystalline material. The product was dissolved in 200 ml of methylene chloride and washed with water (2 x 50 ml). The organic layer was dried over anhydrous potassium carbonate. The methylene chloride was rotary evaporated to yield 7.3467 g (86.41%) of a brown oil.

IR (Neat): 3360(s,br), 2940(s), 1610(m,br), 1510(s)

^{1}H NMR (CDCl$_3$, TMS): 3.38 (s, 5H), 3.68 (dd, 2H), 3.97 (dd, 2H), 6.63 (dd, 4H)

Analysis for C$_9$H$_{13}$NO$_2$ calculated (exp): C, 64.67 (62.47); H, 7.78 (7.88); N, 8.38 (8.04)

1-Benzyloxy-4-(2-methoxyethoxy)benzene[56] (48)

To a 100 ml round bottom flask were placed 10.3433 g (51.717 mmol) of 4-benzyloxyphenol, 10.4431 g (110.51 mmol) of 2-methoxyethyl chloride, 8.4194 g (84.96 mmol) of potassium carbonate and 15 ml of DMF. The flask was fitted with a reflux condenser, and the reaction mixture was heated to 60°C for several hours. The reaction mixture was poured into water and filtered. The precipitate was washed with 10% sodium hydroxide and then water. An ^{1}H NMR spectrum showed some remaining 4-benzyloxyphenol. The product was washed with carbon tetrachloride to remove the 4-benzyloxyphenol. The product was dissolved in 95% aqueous ethanol and precipitated into water.

^{1}H NMR (CDCl$_3$, TMS): 3.43 (s, 3H), 3.74 (dd, 2H), 4.03 (dd, 2H), 5.00 (s, 2H), 6.88 (s, 4H), 7.37 (s, 5H)

Analysis for C$_{16}$H$_{18}$O$_3$ calculated (exp): C, 74.42 (74.39); H, 6.98 (7.05)

4-(2-methoxyethoxy)phenol (49)

Procedure A[57]

The 4-(2-methoxethoxy)aniline (47) (1.6955 g, 10.15 mmol) was dissolved in warm 35% sulfuric acid. The amine bisulfate salt solution was cooled below 5°C. With vigorous stirring, 0.9686 g (14.04 mmol) of sodium nitrite dissolved in 10 ml of water was slowly added to the amine bisulfate solution maintaining the temperature of the solution below 5°C. A few crystals of urea were added to destroy the excess nitrous acid. The solution gave a positive test with alkaline beta-naphthol indicative of a diazonium. The diazonium solution was poured into

a solution of 10.296 g (44.28 mmol) of cupric nitrate dihydrate in 20 ml of water. With rapid stirring, 1.0317 g (7.211 mmol) of cuprous oxide was added. The solution became frothy and orange. The solution gave a negative test for diazonium. The solution was extracted with chloroform (4 x 100 ml), and the organic layer was washed with water (2 x 50 ml). The chloroform was rotary evaporated to yield an orange solid. The orange solid was hot filtered using carbon tetrachloride and decolorizing carbon. The phenol crystallized upon cooling. The white solid was suction filtered. Yield was 0.358 g (21%). A gas chromatograph of the product showed the compound to be essentially pure. The melting point of the solid was 103°C from DSC analysis.

IR (KBr): 3360 (s,br), 2920 (s), 1590 (m,sh), 1510 (s), 1245 (s)

^{1}H NMR (CDCl$_3$, TMS): 3.45 (s, 3H), 3.78 (dd, 2H), 4.04 (dd, 2H), 5.40 (s, 1H), 6.78 (s, 4H)

Analysis for C$_9$H$_{12}$O$_3$ calculated (exp): C, 64.29 (63.52); H, 7.14 (7.05)

Procedure B[58]

To a 50 ml round bottom flask equipped with a magnetic stirrer and dry tube were added 4.5065 g (17.47 mmol) of 1-benzyloxy-4-(2-methoxyethoxy) benzene (48), 30 ml of ethanethiol and 20 cc of boron trifluoride etherate. The reaction mixture was stirred at room temperature overnight. The product mixture was analyzed by G.C. against a known retention time of the product to verify that deprotection had occurred.

Trichloromethyl chloroformate[59] (50)

Into a 100 ml 3-neck round bottom flask fitted with a thermometer, reflux condenser with dry tube, and a coarse fritted gas dispersion tube were placed 32.547 g (0.344 mol) of freshly distilled methyl chloroformate. The mixture was magnetically stirred, and the solution was irradiated with a Spectroline Model B-

100 long wave UV lamp (365 nm). The heat generated warmed the solution slightly. At this point high purity chlorine gas from Matheson was slowly passed into the solution via the fritted bubbler. The flask was placed into a large water bath to serve as a heat sink. The flow of chlorine was adjusted to maintain a reaction temperature between 30 and 35°C. After 6 hours, the chlorine gas was stopped; and at this point the solution had begun to maintain a slight yellow color. The system was then arranged for a vacuum distillation of the product at 20 mm Hg. The fraction collected at 35-40°C showed the strong chloroformate stretching absorption and very little evidence of residual carbon-hydrogen stretching in the infrared spectrum.

IR (Neat): 1810 (s), 1310 (m), 1230 (m), 1100 (s,br)

4-(2-methoxyethoxy)isocyanatobenzene[59] (51)

The 4-(2-methoxyethoxy)aniline (47) was dissolved in 20 ml of diethyl ether. To this was added dropwise concentrated hydrochloric acid with vigorous stirring. A waxy solid precipitated. The ether was rotary evaporated to yeild a tan solid. The amine salt was dried.

To a 100 ml round bottom flask was added 0.6469 g (3.179 mmol) of 4-(2-methoxyethoxy)aniline hydrochloride, 1.488 g (7.515 mmol) trichloromethyl chlorofromate and 20 ml of dry 1,4-dioxane. The flask was fitted with a refluxing condenser and a dry tube. The mixture was heated to 60°C for 20 hours. The 1,4-dioxane was then vacuum distilled at 100 mm Hg leaving a brown residue. After pumping on the residue overnight at room temperature, the infrared spectrum showed the isocyanate stretching absorption at 2270 cm^{-1}.

Bis-4-(2-methoxyethoxy)phenyl carbamate (52)

Procedure A[60]

The 0.083 g (0.494 mmol) of 4-(2-methoxyethoxy)isocyanatobenzene (51) prepared from the reaction of trichloromethyl chloroformate with the amine (47) was used without purification. It was dissolved in 25 ml of carbon tetrachloride and diethyl ether. To this was added 0.1019 g (0.6065 mmol) of 4-(2-methoxyethoxy)phenol (49) and a few drops of pyridine as a catalyst. The mixture was heated to 60°C for 2 hours. The cooled reaction mixture was suction filtered to yield a beige solid. The product was hot filtered and crystallized in carbon tetrachloride to yield a white solid.

Procedure B

Into a 250 ml 3-neck round bottom flask equipped with a condenser and thermometer were placed 150 ml of dry toluene and 1.2191 g of trichloromethyl chloroformate. The solution was cooled below 5°C. At this point 0.2422 g (3.066 mmol) of pyridine was added. A white precipitate formed. The flask was equipped with a dropping funnel containing 0.506 g (3.012 mmol) of 4-(2-methoxyethoxy)phenol (49) in 30 ml of dry toluene and 20 ml of chloroform. The phenol compound was slowly added maintaining the temperature below 5°C. After stirring for a few hours below 0°C, the mixture was stirred at room temperature overnight. The solution became fairly homogeneous. The mixture was again cooled below 5°C, and 1.048 g (13.27 mmol) of pyridine was added. Once again, a white precipitate formed. The addition funnel was filled with 0.519 g (3.108 mmol) of 4-(2-methoxyethoxy)aniline (47) in 30 ml of dry toluene. The amine was slowly added maintaining the temperature below 5°C. The reaction was stirred at ice-water temperatures for 1 hour. The solution was then stirred at room temperatue for 6 hours. The reaction mixture was poured into 250 ml of ice

water. The solution was gravity filtered to yield a beige solid. The product was hot filtered using carbon tetrachloride and then crystallized. The crystals were filtered to yield a white solid. The isolated yield was 0.1118 g (11%). The melting point of the urethane product was found to be 155°C from the DSC.

IR (Deposited film from chloroform): 3310(s), 2920(m), 1740(m), 1705(s), 1610(m), 1550(m), 1510(s)

IR (Nujol): 3320(s), 1740(m), 1712(s), 1612(m), 1550(m), 1510(s)

^{1}H NMR (CDCl$_3$, TMS): 3.44 (s, 6H), 3.77 (dd, 4H), 4.07 (dd, 4H), 7.25 (m, 8H)

Analysis for C$_{19}$H$_{23}$NO$_6$ calculated (exp): C, 63.16 (63.18); H, 6.37 (6.44); N, 3.88 (3.87)

N-Phenyl phenyl carbamate[80] (6)

Inside a dry nitrogen atmosphere box, 5.0 g (53 mmol) of phenol and 6.330 g (53 mmol) of phenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more white precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The white product was hot filtered using carbon tetrachloride and then allowed to crystallize. The white crystals were suction filtered. Yield was 9.9048 g (88%). The melting point from DSC was 126°C.

IR (Deposited film from chlorofrom): 3340 (s), 3060 (w), 1720 (s), 1600 (s), 1570 (s), 1490 (s), 1445 (s)

^{1}H NMR (CDCl$_3$, TMS): 7.2 (m)

^{13}C NMR (CDCl$_3$, TMS): 151.78, 150.58, 137.40, 129.38, 129.08, 125.67, 123.85, 121.66, 118.88

Analysis for $C_{13}H_{11}NO_2$ calculated (exp): C, 73.24 (73.26); H, 5.17 (5.22); N, 6.57 (6.56)

N-(4-Nitrophenyl) phenyl carbamate[60] (27)

Inside a dry nitrogen atmosphere box, 5.0 g (53 mmol) of phenol and 8.723 g (53.2 mmol) of 4-nitrophenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 0.3689 g (2.69%). The melting point from DSC was 163°C.

IR (Deposited film form chloroform): 3320 (m), 1720 (s), 1616 (m,sh), 1600 (m), 1555 (m), 1505 (s)

^{1}H NMR (d_6-Acetone): 7.37 (m, 5H), 7.90 (d, 2H), 8.30 (d, 2H)

Analysis for $C_{13}H_{10}NO_4$ calculated (exp): C, 60.47 (60.42); H, 3.88 (3.90); N, 10.85 (10.80)

N-(4-Methoxyphenyl) phenyl carbamate[60] (28)

Inside a dry nitrogen atmosphere box, 5.0 g (53 mmol) of phenol and 7.925 g (53.2 mmol) of 4-methoxyphenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then

allowed to crystallize. The crystals were suction filtered. Yield was 1.1132 g (8.63%). The melting point from DSC was 157°C.

IR (Deposited film from chloroform): 3340 (m), 1715 (s), 1615 (m,sh), 1590 (m), 1550 (m), 1495 (s)

^{1}H NMR (CDCl$_3$, TMS): 3.59 (s, 3H), 7.20 (m, 9H)

^{13}C NMR: 156.74, 152.72, 152.09, 132.62, 129.97, 125.92, 122.61, 122.61, 120.97, 114.83, 55.61

Analysis for $C_{14}H_{13}NO_3$ calculated (exp): C, 69.14 (69.21); H, 5.35 (5.39); N, 5.76 (5.69)

N-Phenyl 4-nitrophenyl carbamate[60] (16)

Inside a dry nitrogen atmosphere box, 5.0 g (36.0 mmol) of 4-nitrophenol and 4.281 g (36.0 mmol) of phenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 2.3128 g (24.9%). The melting point from DSC was 147°C.

IR (Deposited film from chloroform): 3305 (s), 1710 (s), 1620 (m), 1600 (m), 1530 (s), 1490 (m)

^{1}H NMR (d$_6$-Acetone,TMS): 7.25 (m, 7H), 8.32 (d, 2H)

Analysis for $C_{13}H_{10}N_2O_4$ calculated (exp): C, 60.47 (60.54); H, 3.88 (3.91); N, 10.85 (10.81)

N-(4-Nitrophenyl) 4-nitrophenyl carbamate[60] (29)

  Inside a dry nitrogen atmosphere box, 5.0 g (36.0 mmol) of 4-nitrophenol and 5.899 g (36.0 mmol) of 4-nitrophenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 0.0646 g (0.592%). The melting point from DSC was 227°C.

  IR (Deposited film from chloroform): 3300 (w), 1760 (s), 1750 (s), 1620 (m), 1595 (m), 1555 (s)

  Analysis for $C_{13}H_9N_3O_6$ calculated (exp): C, 51.49 (51.49); H, 2.97 (3.02); N, 13.86 (13.85)

N-(4-Methoxyphenyl) 4-nitrophenyl carbamate[60] (30)

  Inside a dry nitrogen atmosphere box, 5.0 g (36.0 mmol) of 4-nitrophenol and 5.360 g (36.0 mmol) of 4-methoxyphenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 1.0104 g (9.74%). The melting point from DSC was 134°C.

  IR (Deposited film from chloroform): 3340 (m), 1720 (s), 1610 (m), 1590 (m), 1520 (s)

^{1}H NMR (d6-acetone, TMS): 3.78 (s, 3H), 7.06 (d, 2H), 7.53 (dd, 4H), 8.47 (d, 2H), 9.22 (s, 1H)

^{13}C NMR (d6-acetone, TMS): 157.13, 157.01, 151.60, 145.74, 132.01, 125.81, 123.33, 121.38, 114.95, 55.67

Analysis for $C_{14}H_{12}N_2O_5$ calculated (exp): C, 58.33 (58.38); H, 4.17 (4.19); N, 9.72 (9.63)

N-Phenyl 4-methoxyphenyl carbamate[60] (15)

Inside a dry nitrogen atmosphere box, 5.0 g (40.3 mmol) of 4-methoxyphenol and 4.798 g (40.3 mmol) of phenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more white precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 3.5424 g (36.2%). The melting point from DSC was 136°C.

IR (Deposited film from chloroform): 3340 (m), 1715 (s), 1610 (m), 1595 (m), 1545 (m), 1500 (m)

^{1}H NMR (d6-acetone, TMS): 3.73 (s, 3H), 7.2 (m, 9H)

^{13}C NMR (d6-acetone, TMS): 157.94, 152.95, 145.25, 139.64, 129.59, 123.81, 123.42, 119.34, 114.94, 55.75

Analysis for $C_{14}H_{13}NO_3$ calculated (exp): c, 69.14 (69.19); H, 5.35 (5.42); N, 5.76 (5.75)

N-(4-Nitrophenyl) 4-methoxyphenyl carbamate[60] (31)

Inside a dry nitrogen atmosphere box, 5.0 g (40.3 mmol) of 4-methoxyphenol and 6.613 g (40.3 mmol) of 4-nitrophenyl isocyanate were

measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more white precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 0.1814 g (1.56%). The melting point from DSC was 186°C.

IR (Deposited from chloroform): 3340 (m), 2940 (w), 1725 (s), 1615 (m), 1595 (m), 1550 (m), 1505 (m)

^{1}H NMR (d6-acetone, TMS): 3.80 (s, 3H), 7.07 (q, 4H), 7.80 (d, 2H), 8.18 (d, 2H)

^{13}C NMR (d6-acetone, TMS): 158.31, 152.77, 145.98, 144.97, 143.69, 125.70, 123.39, 118.89, 115.10, 55.85

Analysis for $C_{14}H_{12}N_2O_5$ calculated (exp): C, 58.33 (58.26); H, 4.17 (4.22); N, 9.72 (9.66)

N-(4-Methoxyphenyl) 4-methoxyphenyl carbamate[60] (32)

Inside a dry nitrogen atmosphere box, 5.0 g (40.3 mmol) of 4-methoxyphenol and 6.008 g (40.3 mmol) of 4-methoxyphenyl isocyanate were measured into a stoppered 100 ml bottle. The bottle was then removed from the atmosphere box. Then 25 cc of dry toluene were injected into the bottle, followed by 0.5 cc of dry pyridine. The sealed bottle was then shaken until no more precipitate appeared to form. The mixture was allowed to stand for at least 1 additional hour to ensure complete reaction. The product was hot filtered using carbon tetrachloride and then allowed to crystallize. The crystals were suction filtered. Yield was 0.3037 g (2.76%). The melting point from DSC was 180°C.

IR (Deposited from chloroform): 3400 (s,br), 1700 (m,br), 1610 (m), 1540 (m), 1505 (m)

^{1}H NMR (d6-acetone, TMS): 3.79 (s, 3H), 7.00 (m, 6H?), 7.52 (d, 2H)

Analysis for $C_{15}H_{15}NO_4$ calculated (exp): C, 65.93 (65.90); H, 5.50 (5.53); N, 5.13 (5.09)

Syntheses of Functionalized Polyoxyethylene Prepolymers

1,2-Bis(2-(4-Nitrophenoxy)ethoxy)ethane[81] (40)

Into a 500 ml 3-neck round bottom flask were placed 30.297 g (0.2017 mol) of distilled triethylene glycol, 86.214 g (0.6114 mol) of 4-fluoronitrobenzene, and 28.802 g (0.2804 mol) of anhydrous potassium carbonate. The flask was fitted with a reflux condenser and magnetic stir bar. The reaction mixture was heated to reflux with an oil bath at 190°C and kept under an atmosphere of nitrogen. The mixture was heated for 24 hours. The reaction was followed using infrared spectroscopy and was stopped when the appearance of the hydroxyl stretching absorption of triethylene glycol was essentially gone. The reaction mixture was poured into 500 ml of water and stirred vigorously. Initially two layers formed, but after stirring for some time a yellow solid formed. This solid was suction filtered and washed with diethyl ether. The yellow solid was hot filtered using 95% ethanol and allowed to crystallize. The solid was suction filtered and washed with water to yield a light yellow solid. Yield was 49.473 g (62.57%). The melting point was 92-94°C (lit m.p. 96-97°C).

^{1}H NMR: 3.77 (s, 4H), 3.93 (dd, 4H), 4.27 (dd, 4H), 7.01 (d, 4H), 8.23 (d, 4H)

Analysis for $C_{18}H_{20}N_2O_8$ calculated (exp): C, 55.10 (54.97); H, 5.10 (5.09); N, 7.14 (7.11)

1,2-Bis(2-(4-Aminophenoxy)ethoxy)ethane[55] (41)

To a 3-neck 250 ml round bottom flask fitted with a reflux condenser were placed 10.0025 g (25.52 mmol) of 1,2-bis(2-(4-nitrophenoxy)ethoxy)ethane (40), 1.0070 g of 5% palladium on charcoal and 50 ml of absolute ethanol. The flask was flushed and maintained with an atmosphere of nitrogen. Then the mixture was magnetically stirred. Approximately one-half of the 9.67 g (153.5 mmol) of dry ammonium formate was added at once. The mixture was stirred for 1 hour at room temperature. The mixture was then heated to 70°C for 2 hours. At this point, the remainder of the ammonium formate was added and heating was continued for a total of 24 hours. The dark heterogeneous mixture was suction filtered while hot. The supernatant was allowed to cool, and crystallization of the product occurred upon placing the solution in ice water. The crystals were suction filtered and washed with cold ethanol to yield pale yellow needles. Yield was 5.0659 g (59.80%).

The reduction was also performed using a 50% v/v of THF-methanol solvent instead of ethanol. This solvent system allowed the reaction to be run as a more homogeneous solution without the necessity of heating higher than 40°C.

The reaction was monitored using ^{1}H NMR to ensure complete reduction of all nitro functional groups.

^{1}H NMR: 3.74 (s, 4H), 3.82 (dd, 4H), 4.07 (dd, 4H), 6.69 (q, 8H)

Analysis for $C_{18}H_{24}N_2O_4$ calculated (exp): C, 65.06 (65.04); H, 7.23 (7.29); N, 8.43 (8.40)

1,2-Bis(2-(4-Benzyloxyphenoxy)ethoxy)ethane[56] (53)

In a 50 ml flask, 2.1426 g (10.713 mmol) of 4-benzyloxyphenol, 1.0485 g (5.605 mmol) of bis(2-chloroethyl)ether, 1.4881 g (15.016 mmol) of anhydrous potassium carbonate and 25 ml of DMF were refluxed for 7 hours. The reaction

mixture was poured into water and the precipitate was filtered, washed with 2M sodium hydroxide, and then washed with water. The product was recrystallized twice from a 1:1 by volume mixture of methanol and 1,4-dioxane. Yield of white powder after drying was 1.3739 g (49.89%). The melting point was 118°C (lit m.p. 109-112°C).

^{1}H NMR (d6-acetone, TMS): 3.75 (s, 4H), 3.86 (dd, 4H), 4.09 (dd, 4H), 5.03 (s, 4H), 6.89 (s, 8H), 7.42 (s, 10H)

Analysis for $C_{32}H_{34}O_6$ calculated (exp): C, 74.71 (74.61); H, 6.61 (6.66)

1,2-Bis(2-(4-Hydroxyphenoxy)ethoxy)ethane[58] (43)

A mixture of 2.9994 g (5.835 mmol) of 1,2-bis(2-(4-benzyloxyphenoxy)-ethoxy)ethane (53), 8.6406 g (140 mmol) of ethanethiol and 8.3643 g of boron trifluoride etherate were placed in a round bottom flask protected with a drying tube. The mixture was stirred overnight. The mixture remained quite heterogeneous. The mixture was filtered. The precipitate was dissolved in 1,4-dioxane and precipitated into hexane. The precipitate was suction filtered. The product was recrystallized in methylene chloride and suction filtered to yield a white powder.

^{1}H NMR (d6-acetone, TMS): 3.65 (s, 4H), 3.80 (dd, 4H), 6.79(s, 8H), 7.88 (s, 2H)

Analysis for $C_{18}H_{22}O_6$ calculated (exp): C, 64.67 (64.66); H, 6.59 (6.58)

Synthesis of Urethane Capped Functionalized Polyoxyethylene Prepolymers
Bis(1,2-Bis(phenoxyethoxy)ethyl) phenyl carbamate (54)

In a 3 neck round bottom flask fitted with a reflux condenser and dry tube and being maintained under a flow of dry nitrogen were placed 0.2500 g (0.753 mmol) of 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane (41), 0.5090 g (5.0396 mmol) of dry triethylamine and 10 ml of dry diglyme. Then 0.3537 g (2.260 mmol) of

phenyl chloroformate were injected. The next day the reaction mixture was poured into hexane. The precipitate was filtered. The product was washed with water then heated in methylene chloride to remove the 1,2-bis(2-(4-amino-phenoxy)ethoxy)ethane. Yield was 0.2488 g.(57.8%)

Analysis for $C_{32}H_{32}N_2O_8$ calculated (exp): C, 67.13 (67.29); H, 5.59 (5.57); N, 4.90 (4.89)

Bis(1,2-Bis(phenoxyethoxy)ethyl) 4-ethoxyphenyl carbamate (55)

In a 3 neck round bottom flask fitted with a reflux condenser and dry tube and being maintained under a flow of dry nitrogen were placed 4cc of trichloromethyl chloroformate and 10 ml of dry 1,4-dioxane at room temperature. Slowly, 1.0413 g (7.546 mmol) of 4-ethoxyphenol dissolved in 2 ml of 1,4-dioxane were added. The mixture was stirred for 1 hour. Then 0.5 cc of dry pyridine dissolved in 2 ml of 1,4-dioxane were slowly added. Initially, the solution was fairly homogeneous; but a white precipitate formed after 1 hour. At this point, 1.0033 g (3.022 mmol) of 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane (41)and 0.5 cc of dry pyridine dissolved in 10 ml of 1,4-dioxane were slowly added. The solution became heterogeneous. Now 10 ml of DMF were added to help dissolve the mixture. Upon heating to 70°C the solution becaome homogeneous. The temperature was maintained for 1 hour before cooling. The solution was then precipitated into water. A beige solid was suction filtered. The solid was dissolved in DMF and precipitated into methanol. The pale yellow solid was suction filtered. Yield was 0.8473 g (42.5%).

Analysis for $C_{36}H_{40}N_2O_{10}$ calculated (exp): C, 65.45 (65.24); H, 6.06 (6.13); N, 4.24 (4.42)

Synthesis of Poly(oxyethylene-urethane)

Preparation of Polymer (44) from 1,2-bis(2-(4-Hydroxyphenoxy)ethoxy)ethane and 1,2-bis(2-(4-Aminophenoxy)ethoxy)ethane

Procedure A

In a 100 ml 3 neck round bottom flask equipped with a reflux condenser and maintained under a blanket of nitrogen were placed 0.77 g (3.9 mmol) of trichloromethyl chloroformate and 2 ml of dry 1,4-dioxane. Then 0.6538 g (1.96 mmol) of 1,2-bis(2-(4-hydroxyphenoxy)ethoxy)ethane (43) in 10 ml of dioxane were slowly dripped into the reaction mixture at room temperature. Now 0.4 cc of dry pyridine in 2 ml of dioxane was dripped into the mixture. After 15 minutes, an infrared spectrum showed no -OH absorption but did show the two absorptions due to the trichloromethyl chlorofromate and the phenyl chloroformate product. The reaction was almost completely homogeneous. The reaction mixture was heated to 90°C for one hour. After one hour, an IR spectrum at this point showed only the phenyl chloroformate product and no excess trichloromethyl chloroformate. At this point, 0.6494 g (1.96 mmol) of 1,2-bis(2-(4-aminophenoxy)-ethoxy)ethane (41) and 0.4 cc of pyridine in 10 ml of dioxane was added at 90°C. The precipitate that initially formed cleared. There appeared to be two layers. An aliquot was taken after 30 minutes, and an infrared spectrum showed evidence of an X-H stretching absorption at approximately 3500 cm^{-1} and a C=O stretch at 1730 cm^{-1}, while there did not appear to be any NCO nor phenyl chloroformate. Upon cooling, a precipitate formed. Now 10 ml DMF was added to dissolve the product mixture, and this was poured into water. The solid was filtered. The product was redissolved in DMF and reprecipitated into methanol. The precipitate was dried in vacuo to yield 0.8603 g.

Elemental analysis experimental: C, 63.03; H, 5.98; N, 4.10

Procedure B

     In a 100 ml 3 neck round bottom flask equipped with a reflux condenser and maintained under a blanket of nitrogen were placed 2 cc of trichloromethyl chloroformate and 10 ml of dry 1,4-dioxane. Then 0.2499 g (0.753 mmol) of 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane (41) and 0.5 cc of dry triethylamine in 10 ml of dioxane were slowly dripped into the reaction mixture at room temperature. Then 10 ml of DMF was added to dissolve everything. The reaction was heated to 80° C, and the mixture became homogeneous. An IR spectrum showed the presence of formed isocyanate. A small amount of trichloromethyl chloroformate was added to ensure complete conversion of the amine endgroups. An IR spectrum later showed the NCO group but no remaining evidence of amine nor trichloromethyl chlorformate. Then 0.2519 g (0.759 mmol) of 1,2-bis(2-(4-hydroxyphenoxy)ethoxy)ethane (43) in 10 ml of dioxane was slowly added as well as more triethylamine. The reaction became heterogeneous. Then 1 ml of water was added and the solution initially cleared then again became cloudy. Another 5 ml of water was added and again the solution returned to being cloudy. The reaction mixture was filtered, and the flitrate was rinsed with ethanol. The solid was dried in vacuo to yield 0.2904 g.

Thermal Characterization of the Urethane Bond

Differential Scanning Calorimetry Experiments

     The DSC experiments were performed using a Perkin-Elmer DSC-7 interfaced to a Perkin-Elmer Series 7 computer. Prior to the analysis of any of the compounds, the DSC furnace was calibrated for temperature and energy using a pure metal reference standard. A sample of pure indium metal was encapsulated in an aluminum sample pan. This reference sample was then analyzed under the

same experimental conditions as would be used in the analyses of the compounds. The furnace was calibrated each time the experimental conditions of analysis were changed to any large extent.

Thermogravimetric Experiments

The TGA experiments were performed using a Perkin-Elmer TGA-7 interfaced to a Perkin-Elmer Series 7 computer. Prior to performing TGA experiments, the thermobalance was calibrated using a 100 mg mass standard. The thermocouple was calibrated using the Curie temperatures for alumel and nickel standards whose temperatures were respectively, 163°C and 354°C. The Curie temperature is the temperature at which these metal standards lose their magnetic properties. Afterwards, the calibration program was run to calibrate the furnace temperature.

Hot-Stage Infrared Spectroscopy Experiments

The hot-stage infrared (HS-IR) analyses were performed on two infrared spectrometers with different variable temperatue cells. HS-IR experiments were performed using a Fenwall Model 550 Varialble Temperature Controller and infrared cell in conjunction with a Perkin-Elmer Model 281 Spectrophotometer. Additionally, HS-IR experiments were performed using a variable tempreature cell in conjunction with a Bruker IFS 88 Fourier Transform Spectrophotometer equipped with a Bruker FT-IR Microscope with a 15 power objective lens. The HS-IR analyses were performed on dispersions of the compounds in an inert solvent such as mineral oil, diglyme, triglyme and o-dichlorobenzene or on pure samples deposited from a volatile solvent such as chloroform or acetone upon a polished sodium chloride disc. The deposited sample was sealed between NaCl discs with a Teflon spacer. The infrared spectra were then collected as the temperature of the cell was varied.

CHAPTER 3
SYNTHESES OF THE URETHANE COMPOUNDS

To permit the evaluation of the thermally reversible properties of the urethane bond, a synthetic approach for the formation of appropriate urethane compounds was developed. These urethanes could be separated into the following categories: "ideal", substituted, prepolymers, and polymer. These compounds were designed such that the only transition observed would be the reversible dissociation of the urethane bond; no other portion of the compounds would be expected to undergo a transition over the range of temperatures employed in this study. The model aromatic-aromatic urethanes were synthesized and characterized in order to increase our understanding of the reversible properties of the aromatic-aromatic urethane bond that would be found in a poly(oxyethylene-urethane) (44) of the type in Figure 3-1.

-(-OCONH-⬡-(OCH₂CH₂)₃O-⬡-NHCO₂-⬡-(OCH₂CH₂)₃O-⬡-)ₓ-
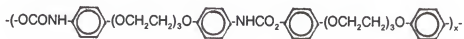
(44)

Figure 3-1. A poly(oxyethylene-urethane) as a thermally reversible urethane.

The Synthesis of an "Ideal" Model Urethane

Since the ultimate objective of this research has been to study the thermally reversible properties of low molecular weight polyoxyethylenes that have been chain extended using an aromatic-aromatic urethane bond, a model

43

$CH_3OCH_2CH_2O$-⟨◯⟩-$NHCO_2$-⟨◯⟩-$OCH_2CH_2OCH_3$

(52)
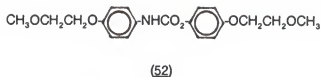
Figure 3-2. Structure of bis-4-(2-methoxyethoxy)phenyl carbamate.

compound was designed that would exhibit chemical and physical properties similar to the urethane polymer system (44). The model compound envisioned as an "ideal" model urethane for this study was bis-4-(2-methoxyethoxy)phenyl carbamate (52), Figure 3-2. This compound (52) contains an aromatic-aromatic urethane bond and ether substituents at the para positions on the aromatic rings similar to the polyoxyethylene chain in Figure 3-1. These ether groups impart similar chemical and physical properties to the model (52) that could be observed in a polyoxyethylene that has been chain extended by an aromatic-aromatic urethane bond. The ether substituent would also be thermally stable and therefore would not undergo thermal transitions under the same conditions at which the urethane bond would thermally dissociate.

$CH_3OCH_2CH_2O$-⟨◯⟩-$N=C=O$ + HO-⟨◯⟩-$OCH_2CH_2OCH_3$

(51)   (49)

$CH_3OCH_2CH_2O$-⟨◯⟩-$NHCO_2$-⟨◯⟩-$OCH_2CH_2OCH_3$

(52)
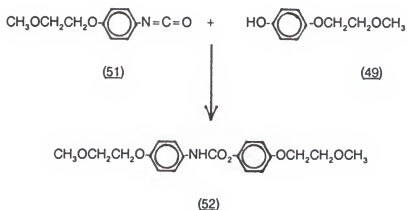
Figure 3-3. Synthesis of bis-4-(2-methoxyethoxy)phenyl carbamate.

Bis-4-(2-methoxyethoxy)phenyl carbamate (<u>52</u>) is unknown, and a synthetic route has been developed. The formation of urethane compounds is generally accomplished by reacting an alcohol with an isocyanate[1]; therefore, the synthesis of bis-4-(2-methoxyethoxy)phenyl carbamate (<u>52</u>) could be achieved by reacting 4-(2-methoxyethoxy)isocyanatobenzene (<u>51</u>) with 4-(2-methoxyethoxy) phenol (<u>49</u>), Figure 3-3. The symmetry of this carbamate (<u>52</u>) as well as the phenol (<u>49</u>) and isocyanate (<u>51</u>) precursors affords the development of a parallel synthetic scheme where the synthesis of the "ideal" model (<u>52</u>) could be achieved through a series of functional group conversions. The approach to the synthesis of the phenol precursor (<u>49</u>) is outlined in Figure 3-4, and the approach to the synthesis of the isocyanate precursor (<u>51</u>) is outlined in Figure 3-5. The synthetic schemes are identical until the final functional group conversions.

In the first step of Figure 3-4, the hydroxyl functionality of 2-phenoxy-ethanol (<u>56</u>) was endcapped with methyl iodide using potassium hydroxide in DMSO, Figure 3-6.[53] The reaction proceeded at room temperature to good yields of a slightly yellow viscous liquid, generally in excess of 90%. The absence of absorption bands in the region of 3500 cm^{-1} in the IR spectrum, Figure 3-7, demonstrates the conversion of the hydroxyl group to the ether group; absorption bands in this region of the infrared spectrum are characteristic of an -OH functional group. The chemical shifts and proton integration in the ^{1}H NMR and ^{13}C NMR spectra are consistent with that expected for 4-(2-methoxyethoxy) benzene (<u>45</u>), Figures 3-8 and 3-9. Endcapping the hydroxyl group with methyl iodide prevents any reaction of this group during later synthetic steps and places an oxyethylene equivalent substituent onto the aromatic ring that can be viewed as an electronic equivalent of a polyoxyethylene chain.
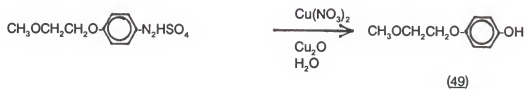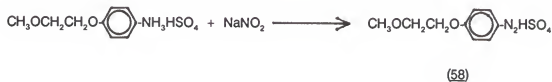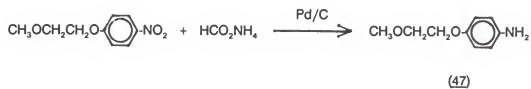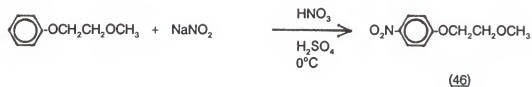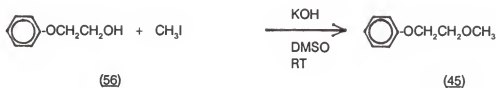
Figure 3-4. Synthesis of 4-(2-methoxyethoxy)phenol.
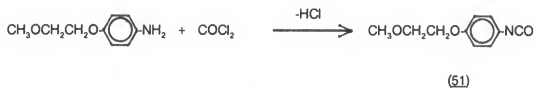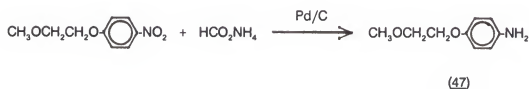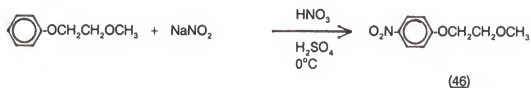
Figure 3-5. Synthesis of 4-(2-methoxyethoxy)isocyanatobenzene.
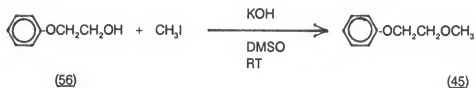
Figure 3-6. Synthesis of 4-(2-methoxyethoxy)benzene.
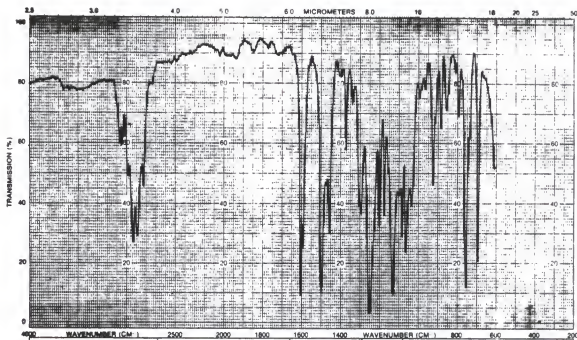
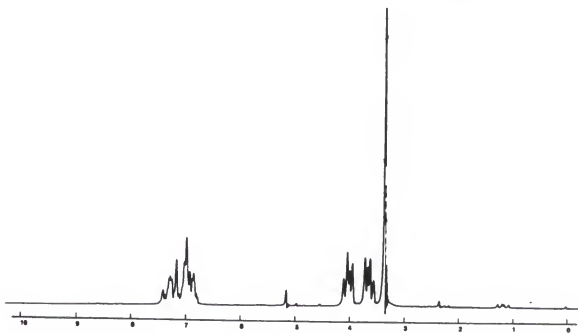Figure 3-7. Infrared spectrum of 4-(2-methoxyethoxy)benzene, neat.

Figure 3-8. 60 MHz ^{1}H NMR of 4-(2-methoxyethoxy)benzene in CDCl$_3$ with TMS.
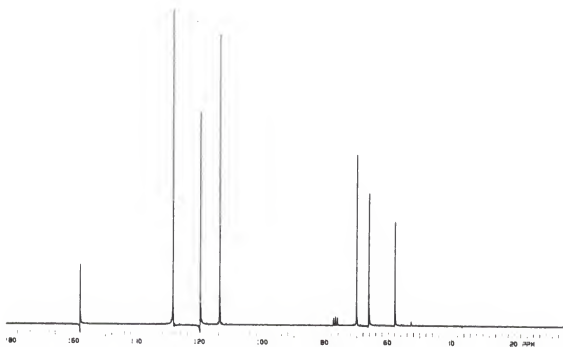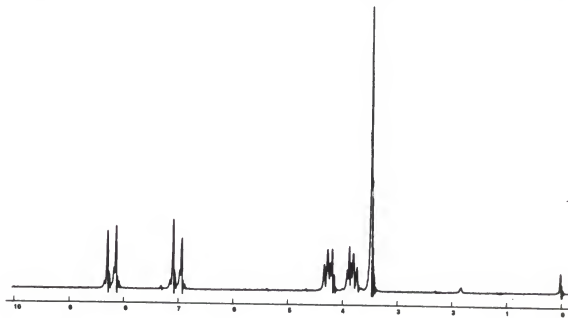
Figure 3-9. 50 MHz ^{13}C NMR of (2-methoxyethoxy)benzene in CDCl$_3$ with TMS.

The second step of the "ideal" model compound (<u>52</u>) synthesis requires the introduction of an appropriate functional group at the position para to the 2-methoxyethoxy substituent already present on the aromatic ring. Since 4-(2-methoxyethoxy)benzene is activated towards electrophilic aromatic substitution, the second group introduced onto the aromatic ring should be a group that will substitute at the para position. Upon its introduction, this group should deactivate the ring towards further substitution, and this substituent also must be capable of being converted eventually to a hydroxyl or isocyanate group. Introduction of a nitro group satisfies the above criteria.

In the nitration of 4-(2-methoxyethoxy)benzene (<u>45</u>), two possible positions exist where nitration can occur, the 2- and 4- positions. Substitution at the 4-
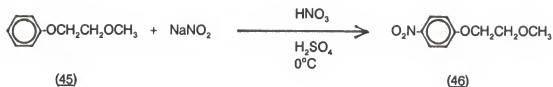
Figure 3-10. Synthesis of 4-(2-methoxyethoxy)nitrobenzene.

position is favored when the nitration reaction is performed in a mixture of nitric acid and sulfuric acid containing sodium nitrite, Figure 3-10.[54] Performing the nitration at $0°C$ assists in limiting the reaction to the introduction of only one nitro substituent, and the use of sodium nitrite favors substitution at the 4- position over the 2- position. The mechanism of the reaction occurred through the formation of an aromatic nitroso compound that is oxidized to an aromatic nitro compound by the nitric and sulfuric acid medium. In fact, during the course of the nitration the reaction mixture changed from a very deep purple color, characteristic of an aromatic nitroso compound, to a red-orange color, characteristic of an aromatic nitro compound. The red-orange needles of 4-(2-methoxyethoxy)nitrobenzene (46) were recrystallized from 95% aqueous ethanol. An advantage of nitrating the aromatic ring was that aromatic nitro compounds could be recrystallized to very high purity, thereby ensuring no presence of any undesirable products. The 4-(2-methoxyethoxy)nitrobenzene was characterized by its melting point of 89-90°C. The IR spectrum contains absorption bands at 1508 and 1335 cm^{-1} assigned to the -NO$_2$ group stretching vibration, Figure 3-11. The ^{1}H NMR and ^{13}C NMR support the structure of a para-nitrated aromatic ether as evidenced by the characteristic nitro aromatic resonance signal, Figures 3-12 and 3-13.
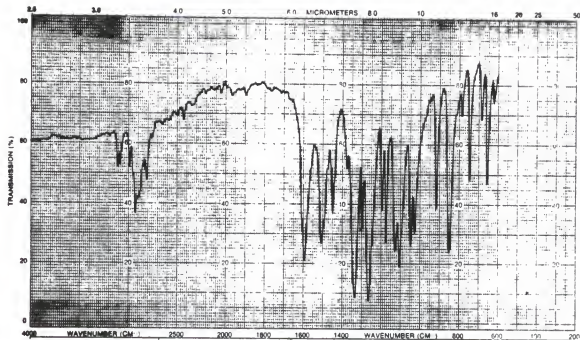
Figure 3-11. IR spectrum of 4-(2-methoxyethoxy)nitrobenzene as a KBr pellet.

Figure 3-12. 60 MHz ^{1}H NMR of 4-(2-methoxyethoxy)nitrobenzene in CDCl$_3$ with TMS.
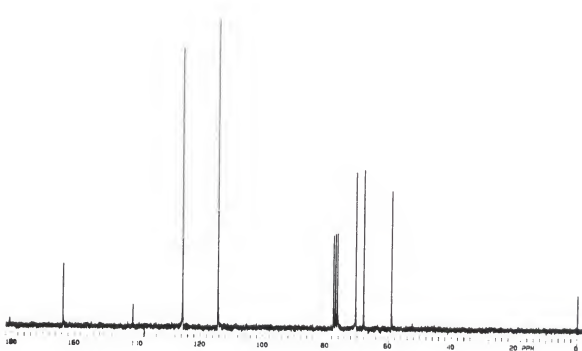
Figure 3-13. 50 MHz ^{13}C NMR of 4-(2-methoxyethoxy)nitrobenzene in CDCl$_3$ with TMS.

Next, the nitro functional group is reduced to an amine group; several reduction procedures were examined.[55,62,63] A reduction procedure requiring anhydrous ammonium formate with a 5% palladium on charcoal catalyst was used, Figure 3-14.[55] The reaction was heated to 50°C overnight, and an aliquot of the reaction mixture was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum indicated no remaining starting nitro compound. After working up the reaction, the yield of the brown liquid amine was 86%. Characterization of 4-(2-methoxyethoxy)aniline (47) showed a broad absorption at 3300-3500 cm^{-1} in the infrared spectrum, Figure 3-15, expected for a primary amine. Additionally, the ^{1}H NMR spectrum gaive evidence for the disappearance of the nitro splitting pattern, Figure 3-16. Some advantages of this procedure were that the reduction
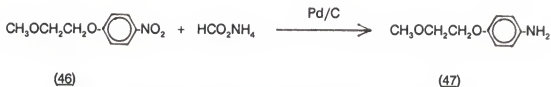
Figure 3-14. Synthesis of 4-(2-methoxyethoxy)aniline.

proceeded at room temperature and could be performed in various inert dry solvents capable of dissolving the nitro starting compound. Additionally, the reaction was monitored easily to ensure complete reduction of all of the nitro compound, which would be advantageous in ensuring complete reduction of a polymeric nitro compound such as α,ω-(nitrobenzene)polyethylene oxide. The reduction was a mild procedure giving it the advantage of being used on a polymeric nitro compound without causing appreciable degradation of the polymer.
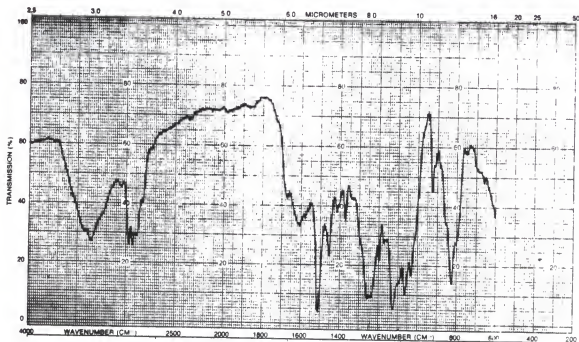
Figure 3-15. IR spectrum of 4-(2-methoxyethoxy)aminobenzene, neat.
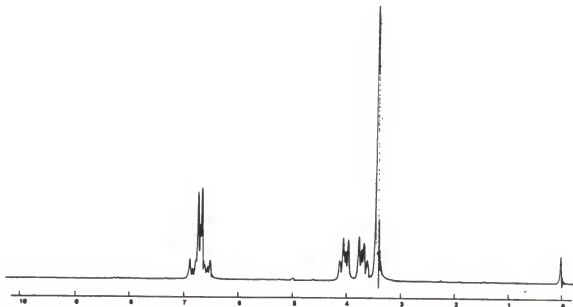
Figure 3-16. 60 MHz ^{1}H NMR or 4-(2-methoxyethoxy)aminobenzene in CDCl$_3$ with TMS.

In the final few steps of Figure 3-4, the amino functionality of (47) was converted to the phenol precursor compound (49) which was needed for the synthesis of bis-4-(2-methoxyethoxy)phenyl carbamate (52). Normally, amines are converted to phenols via the diazonium salt, which is oxidized with boiling sulfuric acid.[64] An alternative oxidation procedure was desirable since hot sulfuric acid could cause degradation of a functionalized polyoxyethylene derivative that will be used later in the synthesis of the poly(oxyethylene-urethane) (44). This alternative procedure replaced the boiling sulfuric acid with a Cu(I) and Cu(II) oxidation system,[57] Figure 3-17. The use of a Cu(I) and Cu(II) oxidation system allowed the conversion of the diazonium (57) to 4-(2-methoxyethoxy)phenol to occur at room temperature. Recrystallization using carbon tetrachloride resulted
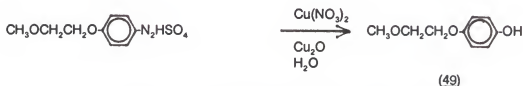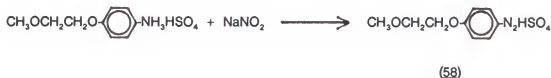
Figure 3-17. Synthesis of 4-(methoxyethoxy)phenol.

in a low yield of 21%. The presence of the para-phenol structure was supported

by the phenolic hydroxyl stretching absorption at 3360 cm^{-1} in the infrared

spectrum, Figure 3-18, as well as in the ^{1}H NMR where the disappearance of the

amine functionality was observed, Figure 3-19.

In order to develop a cleaner and higher yielding synthetic route to 4-(2-

methoxyethoxy)phenol (49), a reaction incorporating a phenol protecting group

was used.[56] This alternative approach eliminated the necessity of the oxidation

step involving either boiling sulfuric acid or the Cu(I)/Cu(II) system. It was during

this oxidation step that various side reactions could occur which would reduce the

yield of the desired phenol product, and these side products could complicate

and cause difficulty in the purification of a polymeric phenol. This alternative route

was a 2 step reaction using a mono-protected bis-phenol followed by subsequent

deprotection of the phenol, Figure 3-20.
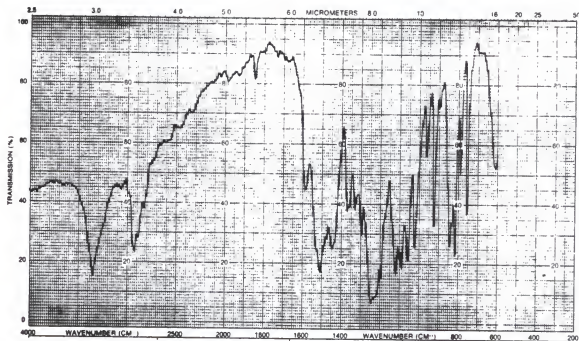
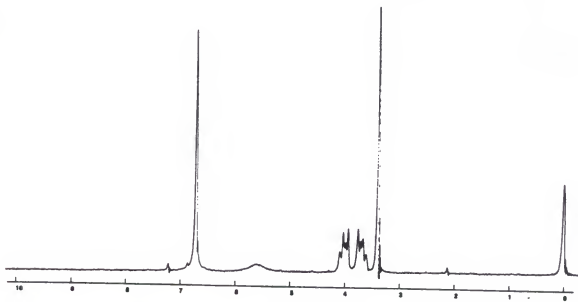Figure 3-18. IR spectrum of 4-(2-methoxyethoxy)phenol in KBr.

Figure 3-19. 60 MHz ^{1}H NMR of 4-(2-methoxyethoxy)phenol in CDCl$_3$ with TMS.
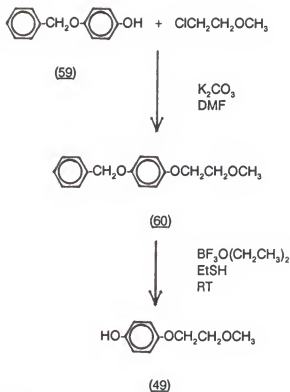
Figure 3-20. Synthesis of 4-(2-methoxyethoxy)phenol via protected phenol group.

In the first step, the reaction of 4-benzyloxyphenol (59) with 2-methoxyethyl chloride was carried out using potassium carbonate in DMF. Characterization using ^{1}H NMR spectroscopy showed a resonance signal at 4.9 ppm with an integration equivalent to the 2 benzyl hydrogens, Figure 3-21.

In the second step of Figure 3-20, deprotection of the phenol group of (60) was accomplished using a reagent system selective for the cleavage of benzyl ethers, boron trifluoride etherate in ethanethiol.[58] The product (49) was easily identifiable by spectroscopic methods and by gas chromatographic analysis. The completion of the reaction could also be determined from peak area integration of the gas chromatogram; therefore, additional quantities of boron trifluoride
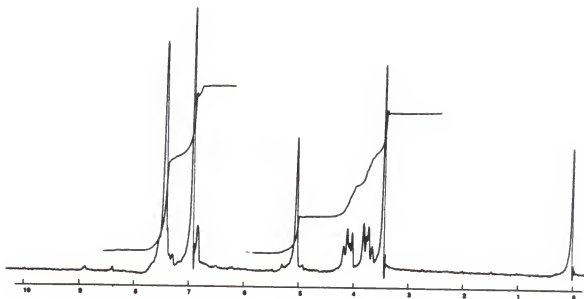
Figure 3-21. 60 MHz ^{1}H NMR of 1-benzyloxy-4-(2-methoxyethoxy)benzene in CDCl$_3$ in TMS.

etherate was added until the deprotection is complete. This ensured that no protected phenol material (60) remained.
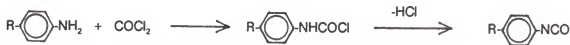

Figure 3-22. Phosgenation of aromatic amines.

4-(2-Methoxyethoxy)aniline (47) was the precursor for both 4-(2-methoxy-ethoxy)phenol (49) and 4-(2-methoxyethoxy)isocyanatobenzene (51), Figure 3-5. A common procedure for the conversion of an aromatic amine to an isocyanate involves the phosgenation reaction of an amine with phosgene,[64,65] Figure 3-22, where the resulting intermediate usually is not isolated but is converted to the isocyanate by the elimination of HCl. Phosgene, owing to it

being a very volatile and toxic gas, would be tedious to use on a repetitious small scale series of reactions; therefore, a substitute for phosgene was desirable. A much more convenient substitute for phosgene was trichloromethyl chloroformate (50), a reagent commonly referred to as "diphosgene." The trichloromethyl chloroformate was synthesized by the photolysis of methyl chloroformate (61) using chlorine, Figure 3-23.[59] The chlorination reaction was continued until the reaction mixture began to retain the slight yellow color of unreacted chlorine, and the purification of the slightly yellow liquid was accomplished by fractional distillation at 20 mm Hg with the product distillate collected between 35-40°C. In Figure 3-24, the IR spectrum of the neat liquid showed an absorption band at 1810 cm^{-1}, characteristic of the carbonyl stretching absorption of trichloromethyl chloroformate. The IR spectrum showed that only a small amount of residual hydrogen containing substance remained as evidenced by the lack of any significant C-H stretching absorption. An advantage in using trichloromethyl chloroformate was that as a liquid it could be handled and measured more easily for small scale reactions, and the higher boiling point of trichloromethyl chloroformate permitted the phosgenation reaction to be carried out at elevated temperatures without the necessity of higher pressures or elaborate reaction vessels.

$$CH_3OCOCl + Cl_2 \xrightarrow[40°C]{h\nu} CCl_3OCOCl$$

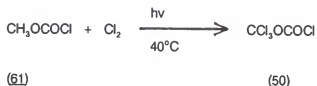(61)   (50)
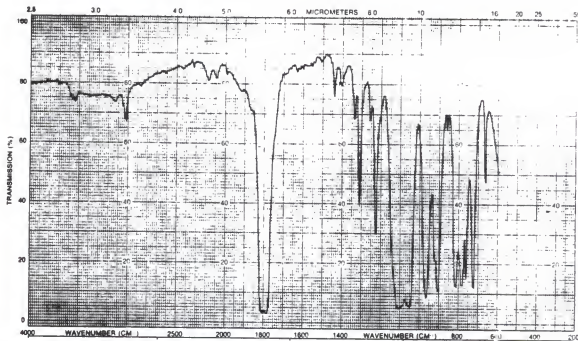
Figure 3-23. Synthesis of trichloromethyl chloroformate.

Figure 3-24. IR spectrum of trichloromethyl chloroformate, neat.

The 4-(2-methoxyethoxy)aniline (47) conversion to 4-(2-methoxyethoxy) isocyanatobenzene was accomplished by first forming the hydrochloride salt (62) and then subsequently reacting the hydrochloride salt with trichloromethyl chloroformate in refluxing dry 1,4-dioxane, Figure 3-25.[59] A brown residue remained upon distillation of the solvent. The infrared spectrum of the residue contained the isocyanate stretching absorption at 2270 cm^{-1}, Figure 3-26.
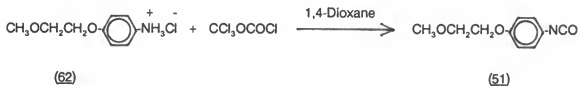

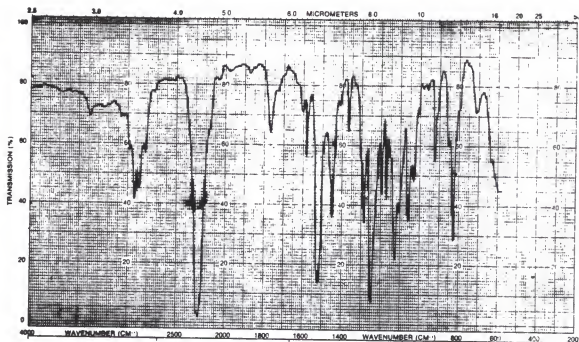Figure 3-25. Synthesis of 4-(2-methoxyethoxy)isocyanatobenzene.

Figure 3-26. IR spectrum of 4-(2-methoxyethoxy)isocyanatobenzene.

The synthesis of the "ideal" model urethane (52) could be accomplished through two different routes using the same starting materials, the only difference being the sequence in which the reactions would be performed, Figure 3-27. In Route 1, the "ideal" model urethane (52) could be formed by first reacting 4-(2-methoxyethoxy)aniline with HCl to form the amine salt before reacting with trichloromethyl chloroformate, and the 4-(2-methoxyethoxy) isocyanatobenzene product (51) would then be reacted with 4-(2-methoxy ethoxy)phenol (49) using pyridine as a catalyst to produce (52). Using Route 1 (Figure 3-27), the urethane (52) was prepared by the addition reaction of 4-(2-methoxyethoxy)isocyanato-benzene, from the reaction of 4-(2-methoxyethoxy)aniline with trichloromethyl chloroformate without purification, with 4-(2-methoxyethoxy)phenol (49) in a

Route 1

$$R = CH_3OCH_2CH_2-$$
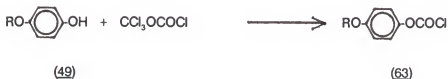
Route 2

$$R = CH_3OCH_2CH_2-$$

Figure 3-27. Synthesis of bis-4-(2-methoxyethoxy)phenyl carbamate.

solvent mixture of carbon tetrachloride and diethyl ether. The white solid bis-4-(2-methoxyethoxy)phenyl carbamate (52) was recrystallized from carbon tetrachloride.

In Route 2 in Figure 3-27, the synthesis involved a reversal of the previous sequence of reactions. The first step involved the reaction of 4-(2-methoxy

ethoxy)phenol (49) with excess trichloromethyl chloroformate to give 4-(2-methoyxethoxy)phenyl chloroformate (63), and this aromatic chloroformate was then reacted with 4-(2-methoxyethoxy)aniline to produce the urethane (52). The reaction of 4-(2-methoxyethoxy)phenol with trichloromethyl chloroformate to yield 4-(2-methoxyethoxy)phenyl chloroformate was monitored by infrared spectroscopy. Characterization of the 4-(2-methoyxethoxy)phenyl chloroformate by infrared spectroscopy showed a carbonyl stretching absorption at 1790 cm^{-1} for the phenyl chloroformate carbonyl as compared to a stretching absorption at 1810 cm^{-1} for trichloromethyl chloroformate. Additional aliquots of trichloromethyl chloroformate were added until all of the phenol was converted. The phenyl chloroformate product (63) was not isolated and upon the removal of any unreacted trichloromethyl chloroformate by distillation was reacted in situ with 4-(2-methoxyethoxy)aniline to produce (52). The isolated yield from this second approach was 21%. The carbonyl stretching absorption of the urethane was observed at 1710 cm^{-1} in the infrared spectrum, Figure 3-28. The ^{1}H NMR spectrum showed the aromatic signals for the 2 aromatic rings of (52), Figure 3-29.

This "ideal" model urethane (52) now possesses a functional group at the para positions on both aromatic rings similar to a repeat unit of ethylene glycol which approximates the aromatic-aromatic urethane bond that can be found in the chain extended low molecular weight oligomers of polyoxyethylene, and this model (52) could be used in the examination of the thermal dissociation properties of the urethane bond. Both routes were used to prepare the urethane (52), and this compound was used to investigate the reversibility as described in chapter 4.
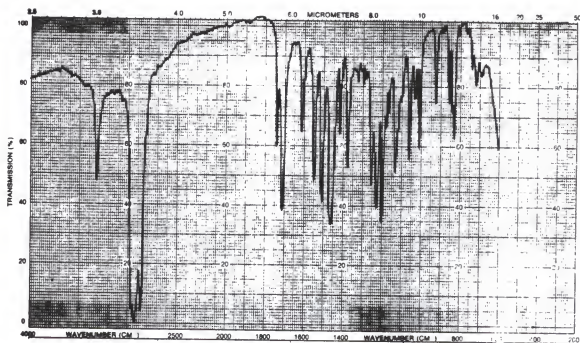
Figure 3-28. IR spectrum of bis-4-(2-methoxyethoxy)phenyl carbamate in Nujol.
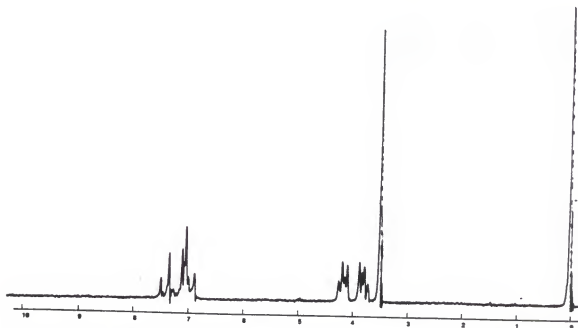

Figure 3-29. 60 MHz ^{1}H NMR of bis-4-(2-methoxyethoxy)phenyl carbamate in CDCl$_3$ with TMS.

The Synthesis of Substituted Model Urethanes

In an effort to better understand the factors affecting the thermal dissociation of the urethane bond in the pure state, a series of substituted aromatic-aromatic model urethanes were synthesized and characterized. These compounds allowed the evaluation of how the presence of different substituents on the aromatic ring affects the dissociation of the urethane bond. Nine model urethanes containing electron-withdrawing, electron-releasing, and hydrogen substituents located at the para position of the aromatic ring of the phenol or isocyanate were synthesized by reacting p-nitrophenol, phenol and p-methoxyphenol with p-nitrophenyl isocyanate, phenyl isocyanate and p-methoxyphenyl isocyanate in all possible combinations, Figure 3-30. Each of these urethanes were synthesized by mixing the respective phenol and phenyl isocyanate in dry toluene and then catalyzing the reaction by adding dry pyridine.[60] Some of the urethanes reacted rather quickly to form a precipitate while others required the application of heat. Each of the urethane products have been identified from their IR spectrum, 60 MHz ^{1}H NMR and 50 MHz ^{13}C NMR spectra, as well as elemental analysis. This series of 9 urethanes has been used in the evaluation of the effect of electron-withdrawing or electron-releasing substituents upon the thermal dissociation of the urethane bond relative to the unsubstituted aromatic-aromatic urethane.

The Synthesis of the Prepolymer Precursors

In addition to studying the thermal dissociation of small model urethanes, a goal of the research was to examine the thermal dissociation of the aromatic-aromatic urethane bond in a polymeric system in the absence of solvent. To this end, it was first necessary to synthesize a polyurethane that would contain the

	R	R'
(6)	H	H
(27)	NO$_2$	H
(28)	OCH$_3$	H
(16)	H	NO$_2$
(29)	NO$_2$	NO$_2$
(30)	OCH$_3$	NO$_2$
(15)	H	OCH$_3$
(31)	NO$_2$	OCH$_3$
(32)	OCH$_3$	OCH$_3$

Figure 3-30. A series of para-substituted aromatic urethanes.

aromatic-aromatic urethane bond but containing no other bonds that would undergo a chemical transformation over the temperature range of reversible dissociation, Figure 3-31. A low molecular weight polyoxyethlyene was directly functionalized through the formation of an aliphatic-aromatic ether bond to produce low molecular weight prepolymers capable of chain extension to form the poly(oxyethylene-urethane) (44), Figure 3-32.
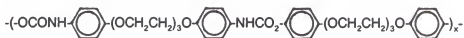
(44)

Figure 3-31. Structure of proposed novel poly(oxyethylene-urethane).

As in the case of the "ideal" model urethane (52), before synthesizing the poly(oxyethylene-urethane) polymer, it was necessary to perform a series of functional group conversions to obtain the requisite bis-aromatic isocyanate (42)
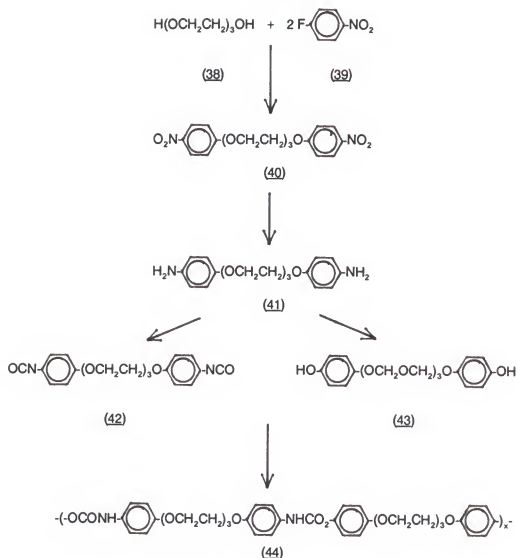
Figure 3-32. Synthesis of chain extended polyoxyethlenes via the aromatic-aromatic urethane bond.

and bis-aromatic phenol (43) precursors. The first step required the

functionalization of low molecular weight polyoxyethylene oligomers, such as 1,2-

bis(2-(4-nitrophenoxy)ethoxy)ethane (40), from the reaction of triethylene glycol

with 4-fluoronitrobenzene (39), Figure 3-33.[61] The reaction was refluxed for 24

hours during which the reaction mixture was analyzed using infrared

spectroscopy. Completion of the reaction was determined when there appeared
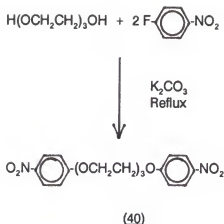
(40)

Figure 3-33. Synthesis of 1,2-bis(2-(4-nitrophenoxy)ethoxy)ethane.

to be very little evidence of an -OH stretching absorption at 3300-3500 cm^{-1} in the IR spectrum. In Figure 3-34, the resonance splitting pattern of a para substituted nitro aromatic compound was observed in the ^{1}H NMR spectrum, as expected from 1,2-bis(2-(4-nitrophenoxy)ethoxy)ethane (40). The yellow solid was recrystallized in 95% aqueous ethanol to yield 63% of the pure nitro compound (40). This ensured that only the α,ω-bis functionalized glycol derivative was obtained, and no mono functionalized derivative was present as a significant impurity. A mono functionalized derivative would interfere with the step polymerization of the isocyanate and phenol prepolymers to yield high molecular weight polymer by serving as an endcapping reactant. The monodisperse nitrated ethylene glycol oligomer (40) was recrystallized to high purity and was completely nitrated at both ends; this was proven by gas chromatography and ^{1}H NMR integration. This ensured that there was no free unreacted alkyl hydroxyl groups that could become incorporated into the final polymers as an aliphatic-aromatic urethane bond.
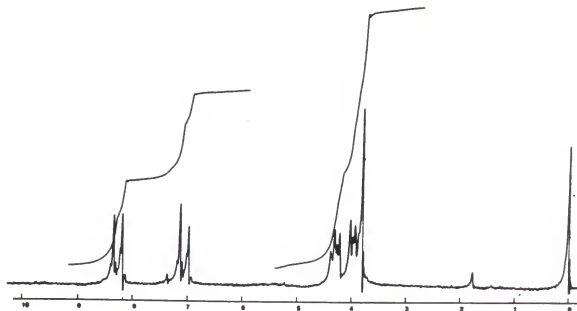
Figure 3-34. 60 MHz ^{1}H NMR of 1,2-bis(2-(4-nitrophenoxy)ethoxy)ethane in CDCl$_3$ in TMS.

Upon purification of the aromatic nitro derivative (40), the nitro endgroups were reduced using ammonium formate with palladium on a carbon catalyst, Figure 3-35.[55] The reduction, which was performed in ethanol at 70°C for 26 hours, was determined to be complete due to the absence of the nitro aromatic resonance signal and the presence of the aromatic amine resonance signal in the ^{1}H NMR spectrum. Also, the reaction progress was followed by gas chromatography. In a solvent system of 50% by volume of THF and methanol, the reduction proceeded at temperatures not exceeding 40°C. The bicomponent solvent system was effective at a lower temperature since the starting aromatic nitro compound was soluble at the lower temperature. Recrystallization from ethanol yielded 60% of pale yellow needles of the desired amine product (41). The ^{1}H NMR in Figure 3-36 provided evidence that the reduction of the aromatic nitro groups to the amine had taken place and that no unreduced nitro groups
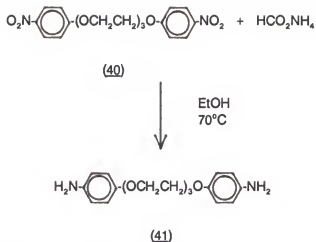
Figure 3-35. Synthesis of 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane.

were evident. The ammonium formate reduction worked well in THF or methanol since the prepolymer was soluble at room temperature. The reduction was monitored using ^{1}H NMR spectroscopy and gas chromatography.
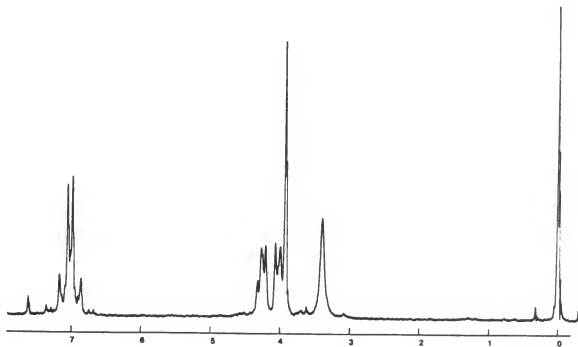

Figure 3-36. 60 MHz ^{1}H NMR of 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane in CDCl$_3$ with TMS.

During the synthesis of the model urethane (52), it was possible to synthesize 4-(2-methoxyethoxy)phenol (49) via a diazonium intermediate; and this phenol was purified from any reaction side products. If the same reaction were used to synthesize 1,2-bis(2-(4-hydroxyphenoxy)ethoxy)ethane (43), undesirable side products and coupling products would present difficulties during purification; therefore, an alternate and more controlled approach utilizing the protected phenol group was used. This route involved the use of a benzyl group to protect the phenol endgroup during the functionalization of the polyoxyethylene. This procedure began with the synthesis of a protected phenol derivative of triethylene glycol, Figure 3-37.[56] The reaction involved the substitution of 4-benzyloxyphenol (59) for the chlorine endgroups of 1,2-bis-(2-chloroethoxy)ethane (64) using anhydrous potassium carbonate in refluxing dimethlyformamide. The reaction mixture was refluxed for 7 hours, and the product was precipitated into water. The protected phenol (53) was recrystallized from a 1:1 by volume mixture of methanol and 1,4-dioxane to give a white powder in 50% yield; a yield higher than would have been expected or achieved via the diazonium route. The melting point was 118°C (lit mp 109-112°C). The ^{1}H NMR spectrum in Figure 3-38
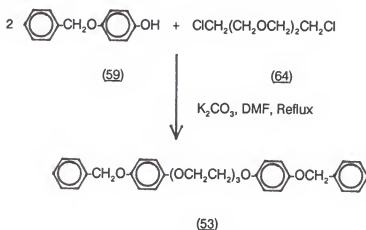

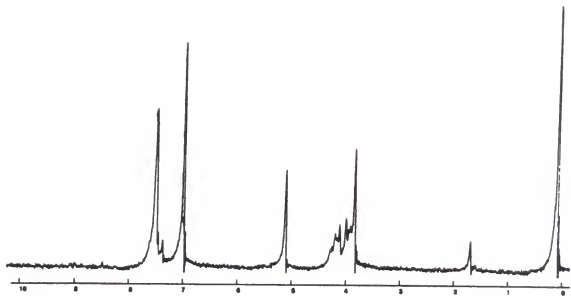Figure 3-37. Synthesis of 1,2-bis(2-(4-benzyloxyphenoxy)ethoxy)ethane.

Figure 3-38. 60 MHz ^{1}H NMR of 1,2-bis(2-(4-benzyloxyphenoxy)ethoxy)ethane in d$_6$-acetone with TMS.
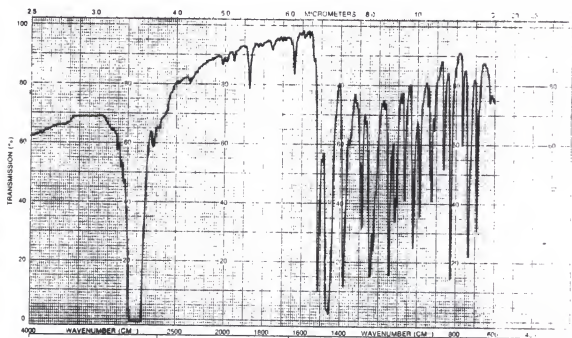

Figure 3-39. IR spectrum of 1,2-bis(2-(4-benzyloxyphenoxy)ethoxy)ethane in Nujol.

showed the presence of the benzyl group, and proton integration supported the functionalization of both ends. In addition, the infrared spectrum did not show any evidence of a hydroxyl stretching absorption, Figure 3-39.

To liberate the phenol endgroups, the benzyl protecting groups had to be removed; and there were several approaches to unprotecting phenols. In the present case there were two unequivalent sites at which cleavage could occur, site A or B in Figure 3-40, producing two different phenols. A reagent that was selective towards cleavage of benzyl ethers was chosen to prevent the possibility of cleavage occurring at site B or to prevent a combination of cleavage at site A at one end while cleaving at site B at the opposite end of 1,2-bis(2-(4-benzyloxy-phenoxy)ethoxy)ethane. The benzyl protecting groups were selectively removed using boron trifluoride etherate in ethanethiol, Figure 3-41.[58] The cleavage reaction was performed at room temperature to yield a white powder recrystallized from methylene chloride. The IR spectrum in Figure 3-42 showed the presence of an O-H stretching absorption due to the removal of the benzyl protecting group. The ^{1}H NMR spectrum and peak assignments in Figure 3-43 demonstrated that the boron trifluoride etherate in ethanethiol was effective as a reagent for the selective cleavage of a benzyl ether protecting group and that cleavage did not occur at the aliphatic ether, site B. There also was no evidence of any remaining benzyl protecting groups.
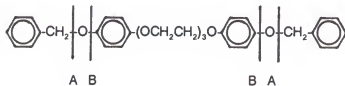

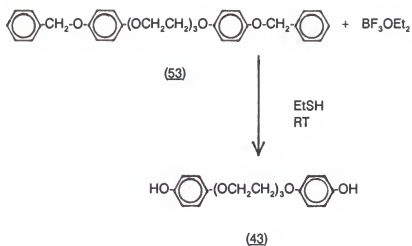Figure 3-40. Selective cleavage of a benzyl protecting group.

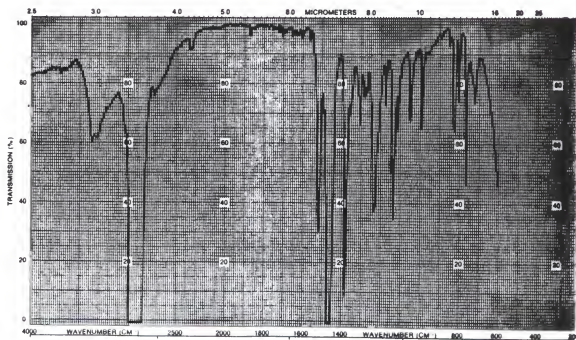Figure 3-41. Synthesis of 1,2-bis(2-(4-hydroxyphenoxy)ethoxy)ethane.

Figure 3-42. IR spectrum of 1,2-bis(2-(4-hydroxyphenoxy)ethoxy)ethane in Nujol.
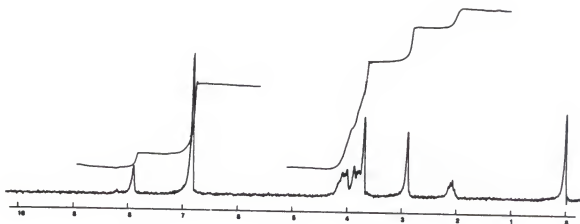
Figure 3-43. 60 MHz ^{1}H NMR of 1,2-bis(2-(4-hydroxyphenoxy)ethoxy)ethane in d$_6$-acetone with TMS.

The prepolymeric precursors, (41) and (43), have been synthesized and were used in the synthesis of a poly(oxyethylene-urethane) (44) discussed later in this chapter.

The Synthesis of the Prepolymeric Urethanes

To make the transition from small model urethane compounds to polyurethanes, two prepolymeric urethanes were prepared. These compounds were prepared by endcapping the prepolymeric bis-amine (41) (or bis-isocyanate equivalent) with either the phenol equivalent (65) or the 4-ethoxyphenol equivalent (66), Figure 3-44. In the first example, 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane was reacted with phenyl chloroformate (65) in dried diglyme with triethylamine to produce the white cyrstalline product, bis(1,2-bis(phenoxyethoxy)ethyl) phenyl carbamate (54). In the second example, 4-ethoxyphenol was reacted with an excess of trichloromethyl chloroformate in 1,4-dioxane to produce 4-ethoxyphenyl

Phenol Capped Prepolymeric Urethane
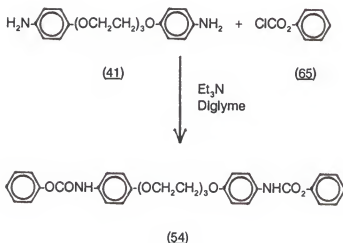
Ethoxyphenol Capped Prepolymeric Urethane
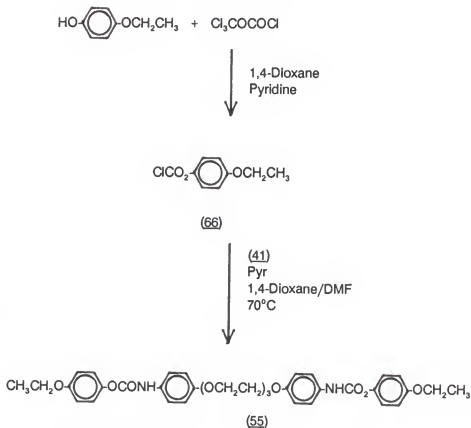

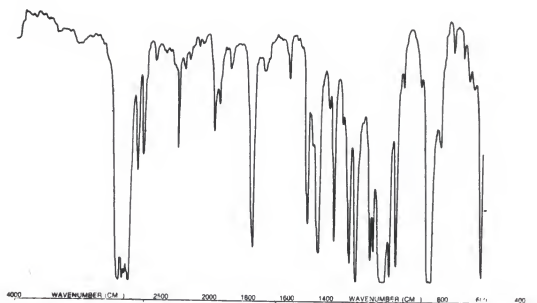Figure 3-44. Preparation of prepolymeric urethanes.

Figure 3-45. IR spectrum of aliquot of the reaction of 4-ethoxyphenol with trichloromethyl chloroformate.
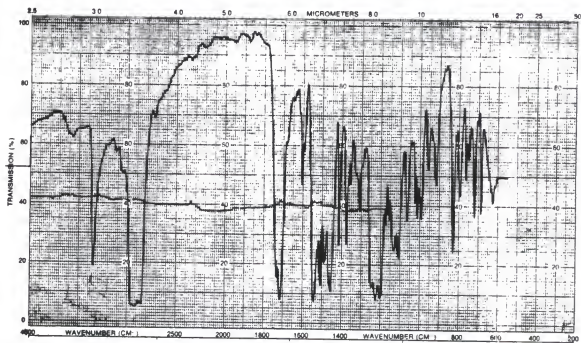

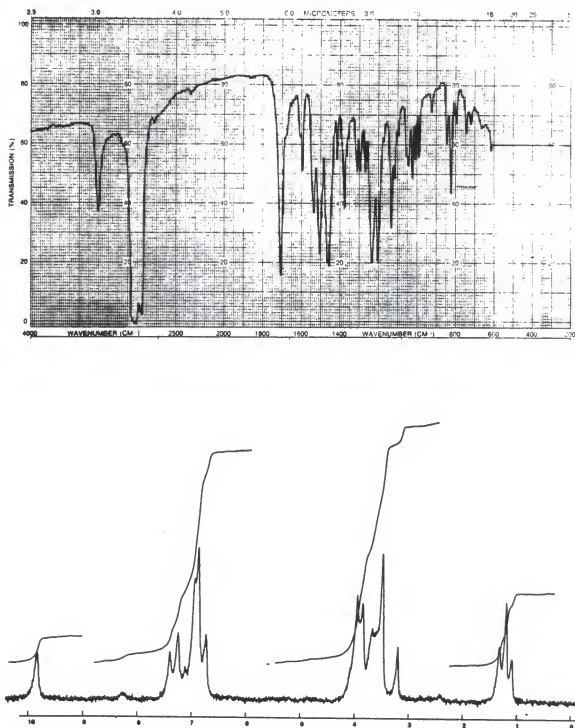Figure 3-46. IR Spectra of bis(1,2-bis(phenoxyethoxy)ethyl) phenyl carbamate.

Figure 3-47. Spectra of bis(1,2-bis(phenoxyethoxy)ethyl) 4-ethoxyphenyl
carbamate: top) IR spectrum, bottom) 60MHz ^{1}H NMR spectrum.

chloroformate (66); and the progress of this step was monitored using IR

spectroscopy, Figure 3-45. The 4-ethoxyphenyl chloroformate was then reacted

in situ with 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane to produce bis(1,2-

bis(phenoxyethoxy)ethyl) 4-ethoxyphenyl carbamate (55). The spectra of these

prepolymeric urethanes are given in Figures 3-46 and 3-47.

The Synthesis of the Poly(oxyethylene-urethane) (39)

At this point in the synthetic approach to the poly(oxyethylene-urethane)

(44) as in the case in the synthesis of the "ideal" model urethane (52), the

formation of the polyurethane became a choice between two routes, Figure 3-48.

The first route was the reaction of the bis-phenol (43) with trichloromethyl

chloroformate followed by the addition of the bis-amine (41) to generate the

polyurethane. The second route was the reaction of the bis-amine (41) with

trichloromethyl chloroformate to generate 1,2-bis(2-(4-isocyanatophenoxy)-

ethoxy)ethane that could be subsequently reacted with the bis-phenol (43) to

prepare the poly(oxyethylene-urethane) (44).

Route 1

HO-◯-(OCH$_2$CH$_2$)$_3$O-◯-OH $\xrightarrow[\text{2) (41)}]{\text{1) CCl}_3\text{OCOCl}}$ Polymer (44)

(43)

Route 2

H$_2$N-◯-(OCH$_2$CH$_2$)$_3$O-◯-NH$_2$ $\xrightarrow[\text{2) (43)}]{\text{1) CCl}_3\text{OCOCl}}$ Polymer (44)
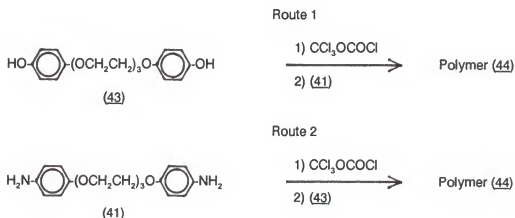
(41)

Figure 3-48. Synthesis of proposed novel triethylene glycol chain extended
polyurethane.
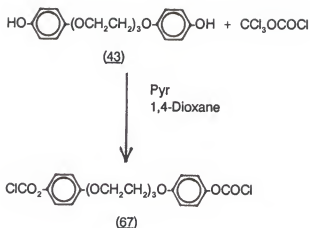
Figure 3-49. Synthesis of 1,2-bis(2-(4-phenoxy)ethoxy)ethyl chloroformate.

In the first approach, 1,2-bis(2-(4-hydroxy-phenoxy)ethoxy)ethane (43) was added to an excess of trichloromethyl chloroformate in 1,4-dioxane under nitrogen, and the reaction was slowly catalyzed by the slow addition of dry pyridine, Figure 3-49. The IR spectrum of the reaction mixture showed no evidence of an -OH stretching absorption but did show the stretching absorptions characteristic of the excess trichloromethyl chloroformate at 1810 cm^{-1} and the substituted phenyl chloroformate (67) at 1790 cm^{-1}. The reaction was heated to 90°C for one hour to remove the excess trichloromethyl chloroformate and to achieve a more homogeneous mixture. After an IR spectrum showed no remaining trichloromethyl chloroformate, a mixture of 1,2-bis(2-(4-aminophenoxy) ethoxy)ethane (41) and pyridine dissolved in dioxane was slowly added at 90°C, Figure 3-50. After 30 minutes, an IR spectrum showed the appearance of an N-H stretching absorption at 3500 cm^{-1} and a C=O stretching absorption at 1730 cm^{-1} suggesting formation of the urethane bond while there was no evidence of unreacted isocyanate nor substituted phenyl chloroformate. The polymer product

ClCO$_2$-⬡-(OCH$_2$CH$_2$)$_3$O-⬡-OCOCl + (41) $\xrightarrow[\text{1,4-Dioxane}]{\text{Pyr}}$ Polymer (44)

(67)
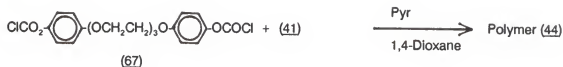
Figure 3-50. Synthesis of triethylene glycol chain extended polyurethane using 1,2-bis(2-(4-phenoxy)ethoxy)ethyl chloroformate.

(44) was isolated from the reaction by precipitation from DMF into methanol to yield 0.8603 g of product.

In the second approach, a mixture of 1,2-bis(2-(4-aminophenoxy) ethoxy)ethane (41) and dry triethylamine was slowly added to excess trichloromethyl chloroformate in dry 1,4-dioxane at room temperature under nitrogen, Figure 3-51. Since the reaction had become heterogeneous, 10 ml of dry DMF were added; and the reaction was heated to 80°C. An IR spectrum showed the presence of the substituted isocyanate. Upon formation of the 1,2-bis(2-(4-isocyanatophenoxy)ethoxy)ethane (42), the bis-phenol (43) and triethylamine in 1,4-dioxane was slowly added, Figure 3-52. The polymer product was isolated by precipitation into water, rinsing the precipitate with ethanol and drying in vacuo to yield 0.2904 g of product.

(41) + CCl$_3$OCOCl $\xrightarrow[\text{2) 80°C}]{\text{1) Et}_3\text{N; 1,4-Dioxane}}$ OCN-⬡-(OCH$_2$CH$_2$)$_3$O-⬡-NCO

(42)
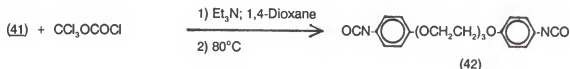
Figure 3-51. Synthesis of 1,2-bis-(2-(4-isocyanatophenoxy)ethoxy)ethane.

Figure 3-52. Synthesis of the triethylene glycol chain extended polyurethane using 1,2-bis-(2-(4-isocyanatophenoxy)ethoxy)ethane.

The syntheses of the model and polymeric urethanes being accomplished, it was then necessary to determine the reversible nature of the urethane bond. The initial syntheses of the urethane compounds have been accomplished in most cases using solution reactions. The reversible nature of these urethanes has been studied under a variety of conditions as described in chapter 4.

CHAPTER 4
THERMAL CHARACTERIZATION OF MODEL AROMATIC URETHANES

As discussed in Chapter 1, the urethane bond is capable of undergoing a thermally reversible dissociation. In the case of an aromatic-aromatic urethane bond, reversible dissociation produces the corresponding isocyanate and phenol, Figure 4-1; and at elevated temperatures, this dissociation can occur without the necessity of an added catalyst. Most of the earlier studies reported in the literature have focused on the dissociation properties of urethanes in solution. However, the applications of urethanes generally do not involve solvents; therefore, it is important to understand how the thermal properties would differ under bulk conditions. In this research, the thermally reversible properties of the aromatic-aromatic urethane bond were studied using several techniques: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and hot-stage infrared spectroscopy (HS-IR). All of these techniques allowed for the characterization of the compounds in the bulk state. Of these techniques, HS-IR proved to be the most informative.

Figure 4-1. Dissociation of aromatic urethane.

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) experiments were conducted in an effort to quantitatively determine the thermally reversible properties of the "ideal" and substituted model aromatic urethane compounds. DSC is a thermoanalytical technique that can be used to characterize the endothermic and exothermic properties of materials.

The DSC experiments were performed on a Perkin-Elmer DSC-7 which is of the power compensated type; and in this arrangement, the temperature of the sample is maintained equal to the temperature of a reference by supplying heat to the sample or reference material. The amount of heat required to maintain this isothermal condition between the sample and the reference is recorded as a function of temperature or time. This produces a measurement of the enthalpy of a physical or chemical transition; therefore, any process that involves changes in enthalpy or specific heat will produce a change in the curve of the DSC scan.[66,67] "The applicability of DSC to condensed-phase systems is almost universal."[67, p. 849] Mass gained or lost during a reaction or transition changes the heat capacity and produces errors in the baseline subtraction. In the case of an addition reaction such as urethane formation, there is no production of a small molecule that would easily be lost from the system; therefore, DSC can be used to study the reversible formation of urethanes. A few of the advantages of using differential scanning calorimetry for evaluating the thermally reversible properties of the aromatic urethane bond are: 1) the analysis of very small samples, 2) the performance of rapid experiments, 3) the analysis of samples in various physical and chemical states and 4) the direct measurement of the enthalpy of the endothermic and exothermic transitions. The DSC measures all enthalpic events, e.g., chemical

reactions and physical transitions, so that the interpretation of the reaction of interest may be obscured by side reactions.[67]

In differential scanning calorimetry experiments, a sample of the urethane compound is sealed in an aluminum DSC pan at room temperature and heated at a controlled rate, e.g. $20°C$ per minute. During the heating of the urethane compound, the nature of the DSC curve is observed; and it is anticipated that after the sample has melted a second endotherm might be observed in the DSC curve. If complete dissociation occurs over a small temperature range, this endotherm might result from the complete dissociation of the urethane bond to isocyanate and phenol in Figure 4-1. Upon cooling, two exotherms might be observed in the DSC curve due to the reaction of the isocyanate and phenol to reform the urethane bond (the reverse of the previous reaction) and also due to crystallization of the urethane. The enthalpies of the endothermic dissociation (the forward reaction) and of the exothermic formation (the reverse reaction) of the urethane might be used to determine the degree of dissociation and reversibility of the urethane. The area under these two thermal transitions might correspond to the enthalpies of the two reactions; and by the principle of microscopic reversibility, the enthalpies of the two reactions should be equal for a completely reversible reaction.

If dissociation occurs over a very broad temperature range, however, a clear second endotherm due to the reversal reaction possibly would not be observed; instead, a broad continuous change in the slope of the baseline would be observed due to the equilibrium nature of the reaction. In a true equilibrium reaction rather than a reversible reaction, the equilibrium would shift to the right in Figure 4-1, thereby producing a slow continuous increase in the number of molecules in the closed system giving rise to a change in the heat capacity of the

system, and this change would be observed only as a shift in the baseline. If the equilibrium constant is linear with respect to temperature, only a linear change in the slope of the baseline would be observed. If other side reactions occur, changes in the slope of the baseline would be observed. Such data could provide useful information regarding the kinetics of the reversible reaction and could provide the information necessary to determine if such a reaction might be viable in a bulk process.

Differential scanning calorimetry experiments were conducted to determine the enthalpies of the forward and reverse reactions involved in the thermally reversible reaction of the "ideal" and substitued model urethane compounds. During the initial heating scan of N-phenyl phenyl carbamate (6) at 10°C/min, the only observed transition was an endothermic transition due to melting of the urethane sample at 127°C, Figure 4-2. There was no evidence of any other endothermic transitions to demonstrate that dissociation had occurred during the heating to 150°C. The fact that only one endotherm was observed upon heating apparently demonstrated that equilibrium conditions were established rather quickly, thereby offsetting any observation of endotherms or exotherms due to the reaction itself. On reheating the quenched sample, two endotherms (one for the phenol and one for the urethane) were observed providing evidence that dissociation of the urethane bond in (6) had begun.

Similar melting curves were observed during the initial melting of N-4-methoxyphenyl 4-nitrophenyl carbamate (30). From an examination of Hoshino's proposed dissociation mechanism as well as earlier solution experiments[8-12], this carbamate (30) would be expected to have a greater propensity towards dissociation since the electron releasing methoxy group would stabilize the isocyanate moiety while the nitro group would decrease the nucleophilicity of the
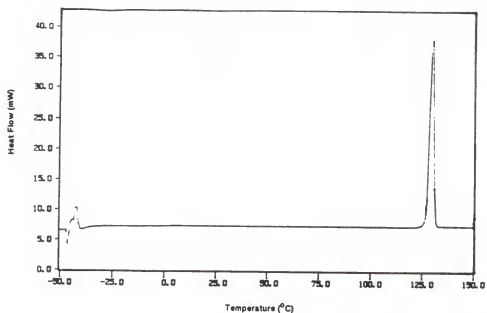
Figure 4-2. DSC curve for the heating of N-phenyl phenyl carbamate at 10°C/min under nitrogen.
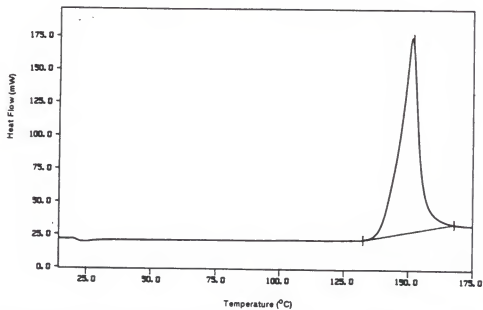

Figure 4-3. DSC scan of N-4-methoxyphenyl 4-nitrophenyl carbamate at 50°C/min in nitrogen.

phenol. A small sample of N-4-methoxyphenyl 4-nitrophenyl carbamate (30) was scanned at a rate of 50°C/min through the melting point up to 175°C, Figure 4-3. The sample was heated rapidly in an effort to create a non-equilibrium condition, but with no success. As in the case of N-phenyl phenyl carbamate (6), only one endotherm was observed at 137°C due to the melting of the urethane. The melted N-4-methoxyphenyl 4-nitrophenyl carbamate (30) was cooled at a rate of 10°C/min to observe either the reformation reaction or the crystallization of the individual components of the dissociation system. Only one exotherm was observed at 101°C, Figure 4-4. The sample was reheated to 175°C; and during this scan, two distinct endotherms were observed, Figure 4-5. The first endotherm occurred at 86°C, corresponding to the melting of the p-nitrophenol from dissociation, and the second endotherm occurred at 146°C, corresponding to the urethane. A subsequent cooling run from 175°C to 25°C at 10°C/min also
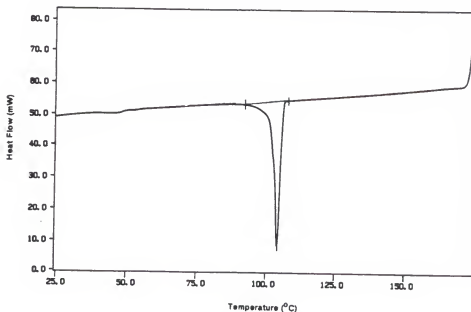

Figure 4-4. DSC scan of cooling N-4-methoxyphenyl 4-nitrophenyl carbamate at 10°C/min in nitrogen.
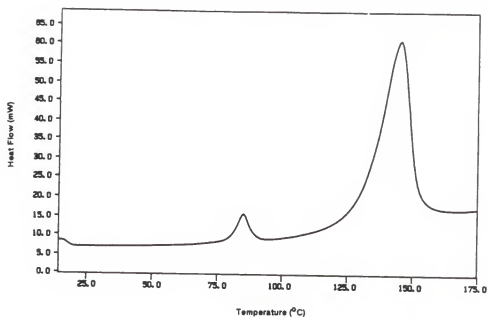
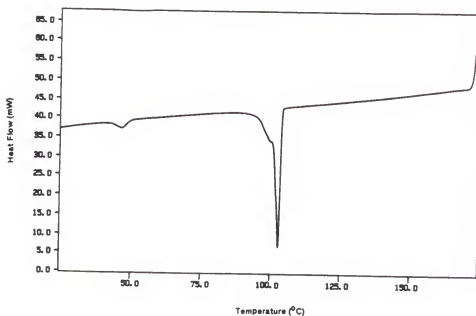Figure 4-5. DSC scan of reheating N-4-methoxyphenyl 4-nitrophenyl carbamate at 50°C/min in nitrogen.

Figure 4-6. DSC scan of a subsequent cooling of N-4-methoxyphenyl 4-nitrophenyl carbamate in nitrogen.

showed two exotherms, Figure 4-6. The first exotherm occurred at 104°C, corresponding to the urethane, and the second exotherm occurred at 47°C, corresponding to the p-nitrophenol. Further reheating continued to show two endotherms. Only two endotherms were observed since the 4-methoxyphenyl isocyanate that would form would be a liquid over the temperature studied. This pattern was reproduced in other heating and cooling experiments providing evidence that dissociation had occurred during heating.

Differential scanning calorimetry experiments were continued using the "ideal" model urethane, bis-4,4'-(2-methoxyethoxy)phenyl carbamate (52). A slow heating rate of 1°C/min was used to ensure that the sample was maintained at thermal equilibrium. The only observed transition was the endothermic melting of the sample at 155°C, Figure 4-7. The quenched sample was reheated at a rate of 20°C/min where a faster heating rate was used to analyze the product of the first heating while minimizing any of the urethane formation reaction. During this second heating of (52), three endotherms were observed, Figure 4-8. All three peaks are endotherms assigned to the melting of the individual components in the sample. The first peak at 87°C represents the melting point for the 4-(2-methoxy-ethoxy)phenol. The endotherm at 131°C represents the melting point of the 4-(2-methoxyethoxy)isocyanatobenzene generated through dissociation of the "ideal" model urethane (52), and the peak at 142°C is the melting of the remaining undissociated urethane compound (52). The melting point of the remaining undissociated carbamate (52) was depressed from the melting point of the pure urethane at 155°C due to the presence of the phenol and isocyanate from dissociation.
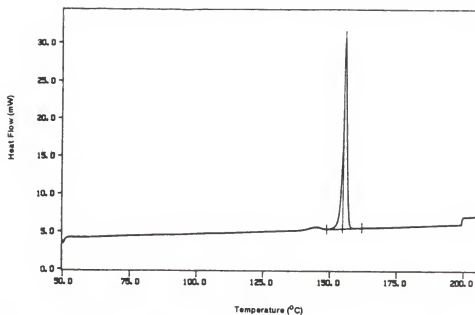
Figure 4-7. DSC curve for the heating of bis-4-(2-methoxyethoxy)phenyl carbamate at 1°C/min under nitrogen.
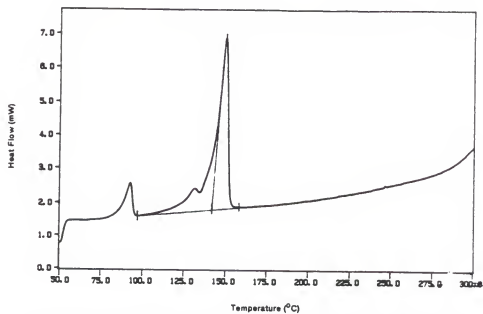

Figure 4-8. DSC curve for the subsequent heating of bis-4-(2-methoxyethoxy)phenyl carbamate at 20°C/min under nitrogen.

Other DSC experiments were attempted in which the rates of heating were as slow as 0.1°C/min and as fast as 50°C/min. These experiments were conducted to evaluate the rate of the forward and reverse reactions. The slow heating rates were used to ensure that the sample was given time to dissociate, while the faster heating rates were used to overheat the sample to observe the relaxation of the dissociation. There was still no apparent direct observation of urethane dissociation during the dynamic heating or cooling cycles.

Further DSC experiments were conducted for N-phenyl phenyl cabamate (6) in an effort to determine whether the change in ΔH for the melting transition of undissociated urethane could be correlated with the extent of dissociation. In attempting this, the sample was scanned to a temperature above the melting point and maintained at this temperature for 30 minutes to ensure the establishment of equilibrium. The sample then was cooled quickly in the DSC pan, and the sample was rescanned whereby on each successive scan the annealing temperature was increased as shown in Table 4-1. No apparent trend for ΔH and onset temperature was observed.

Table 4-1. Changes in Heat of Fusion as a Function of Annealing
Temperature for N-Phenyl Phenyl Carbamate.

Onset Temp (°C)	ΔH (J/g)	Anneal Temp (°C)
117	103	135
126	129	140
116	95	145

The onset temperatures and heats of fusion for the "ideal" (52) and substituted urethane compounds are summarized in Table 4-2. While these experiments showed that a reversal reaction was being observed, quantitative data could not be extracted from the DSC experiments. Absolute heats of fusions

cannot be determined for these compounds, making it impossible to determine the concentrations of the three components.

Table 4-2. Summarized DSC Data for the Model Urethane Compounds.

	Urethane	Onset Temp ($^{\circ}$C)	ΔH (J/g)	Heating Rate ($^{\circ}$C/min)
(6)	PhNHCO$_2$Ph	125	141	20
(27)	O$_2$NPhNHCO$_2$Ph	164	114	10
(28)	CH$_3$OPhNHCO$_2$Ph	157	144	10
(16)	PhNHCO$_2$PhNO$_2$	149	143	100
(29)	O$_2$NPhNHCO$_2$PhNO$_2$	227	165	10
(30)	CH$_3$OPhNHCO$_2$PhNO$_2$	137	149	50
(15)	PhNHCO$_2$PhOCH$_3$	136	118	10
(31)	CH$_3$OPhNHCO$_2$PhOCH$_3$	187	119	10
(32)	O$_2$NPhNHCO$_2$PhOCH$_3$	180	149	10
(52)	"Ideal" Urethane	155	125	1

Thermogravimetric Analysis

Complementary to the differential scanning calorimetry studies, thermogravimetric analyses were also performed on the model urethanes. Thermogravimetric analysis (TGA) is a technique whereby the weight of a sample is recorded as a function of temperature, and TGA can provide information on degradation mechanisms via percent loss of mass as a function of temperature.[66,67] In this technique, a small amount of material is placed in a platinum cup suspended from the arm of a micro-balance. The sample is placed inside a furnace and is heated under a controlled atmosphere, either an inert or reactive gas. Upon heating, the change in the mass is recorded as a function of temperature.

A discussion of the thermal processes occurring during dissociation of the urethane is warranted to understand the thermal transitions which might be observed during thermogravimetric analysis of urethane compounds. Initially the

sample is only the urethane, but as dissociation proceeds the sample becomes a three component mixture consisting of an isocyanate, a phenol and any remaining undissociated urethane; and upon complete dissociation, the sample becomes a two component mixture consisting of an isocyanate and a phenol with no remaining urethane. The shape of the TGA curve will be dependent upon at what temperature vaporization of any material occurs and at what temperature dissociation occurs. Examples of possible theoretical weight loss curves are shown in Figure 4-9.

If dissociation is complete at a relatively low temperature, the system might contain only 2 components, the isocyanate and the phenol. The curve would either show only one weight loss transition if the boiling point and rate of evaporation of the phenol and isocyanate are comparatively equal, case A in Figure 4-9. If the boiling point and rate of evaporation of the phenol and isocyanate vary significantly, the TGA curve might show two clear weight loss transitions corresponding to the evaporation of the phenol and isocyanate separately, case B in Figure 4-9.

If dissociation does not occur nor does any other degradation process, only one weight loss transition would be observed in the TGA curve with the onset of the weight loss corresponding to the vaporization of the undissociated urethane compound. For the case where dissociation of the urethane has occurred but in which dissociation is not complete prior to reaching a temperature where the vaporization of either the phenol or isocyanate begins, several shapes of TGA curves could result ranging from a single weight loss transition to three weight loss transitions, cases A and C in Figure 4-9.

In order to investigate these possibilities, TGA experiments were undertaken to determine if dissociation was occurring at higher temperatures as
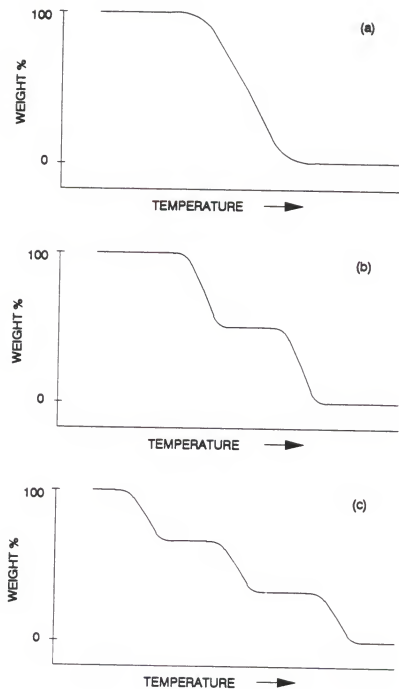
Figure 4-9. Theoretical TGA weight loss curves.

well as to examine the dissociation for any additional type of decomposition reaction that would interfere with a completely reversible reaction. These TGA experiments were performed on each of the small model aromatic urethanes, and the curves generally showed only one continuous weight loss transition. A TGA experiment was first performed on N-phenyl phenyl carbamate (6) at 5°C/min; and only one continuous weight loss transition was observed with an onset of weight loss at 150°C, Figure 4-10. A slower heating rate was also used since it was felt that the boiling points of the formed phenol (5) and phenyl isocyanate (4), 180°C and 163°C respectively, were comparatively close such that the two components could not vaporize separately. Again, only one weight loss transition was clearly observed with no observable changes in the rate of vaporization that would indicate separate vaporization of two or more components.
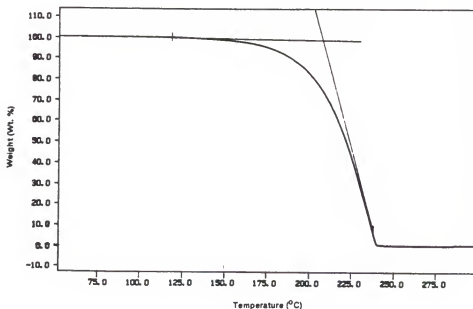
Figure 4-10. TGA curve for N-phenyl phenyl carbamate heated at 5°C/min in nitrogen.
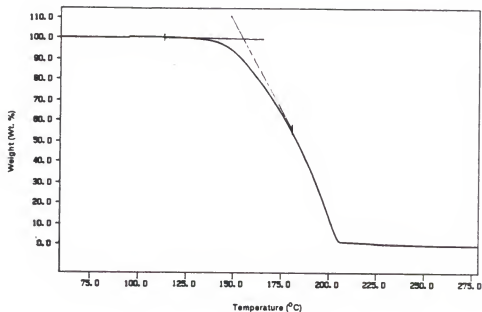
Figure 4-11. TGA curve for N-4-methoxyphenyl 4-nitrophenyl carbamate at 5°C/min in nitrogen.

Another TGA experiment was attempted on N-4-methoyxphenyl 4-nitro-phenyl carbamate (30). The boiling points for 4-nitrophenol and 4-methoxyphenyl isocyanate are both in excess of 200°C, and these temperatures might have allowed a significant amount of dissociation to occur before vaporization of either of these components should begin. Nonetheless, only one continuous weight loss transition was observed to occur at 134°C, Figure 4-11.

However, when TGA experiments were performed on urethanes (27), (29) and (32) synthesized from 4-nitrophenyl isocyanate, two weight loss transitions were observed. The first transition involved the loss of approximately 90% of the weight, whereas the last 10% was lost in the range of 350-450°C. A typical scan
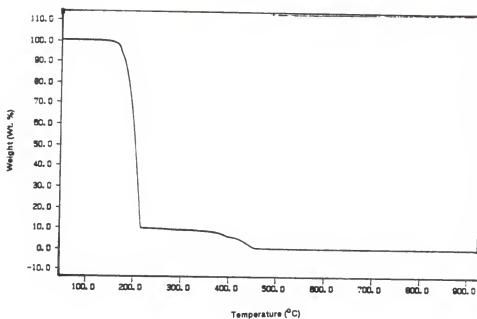
Figure 4-12. TGA curve for N-4-nitrophenyl phenyl carbamate at 10°C/min in nitrogen.

for these urethanes is shown in Figure 4-12. The latter transition could result from the decomposition of carbodiimide formed from 4-nitrophenyl isocyanate at elevated temperatures.

These TGA experiments suggested that the urethane bond was not completely dissociated below 200°C since there was no evidence of multiple transitions. The data for the TGA experiments is summarized in Table 4-3. These TGA experiments provided evidence that dissociation was occurring, but quantitative data could not be directly obtained due to the overlapping of the weight loss transitions for the urethane, isocyanate and phenol.

Table 4-3. Summarized Onset of Weight Loss TGA Data for the Model Aromatic Urethanes

		Heating Rate		Phenol	Isocyanate
	Urethane	1°C/min	10°C/min	bp(°C)	bp(°C)
(6)	PhNHCO$_2$Ph	134	208	180	163
(27)	O$_2$NPhNHCO$_2$Ph	164	185	180	137[a]
(28)	CH$_3$OPHNHCO$_2$Ph	156	169	180	106[b]
(16)	PhNHCO$_2$PhNO$_2$	141	151	279[c]	163
(29)	O$_2$NPhNHCO$_2$PhNO$_2$	164	198	279[c]	137
(30)	CH$_3$OPhNHCO$_2$PhNO$_2$	136	152	279[c]	106
(15)	PhNHCO$_2$PhOCH$_3$	141	170	243	163
(31)	O$_2$NPhNHCO$_2$PhOCH$_3$	184	202	243	137
(32)	CH$_3$OPhNHCO$_2$PhOCH$_3$	185	192	243	106

a) b.p. at 11 mm Hg. At atmospheric pressure b.p. estimated approx. 260°C
b) b.p. at 16 mm Hg. At atmospheric pressure b.p. estimated approx. 230°C
c) decomposes at this temperature

Characterization of the Aromatic-Aromatic Urethanes Using Hot-Stage Infrared Spectroscopy

In an effort to obtain direct evidence for the dissociation of the urethane bond in the bulk state, spectroscopic techniques were evaluated as to their utility in the characterization of the thermal properties of the urethane bond. The spectroscopic technique might be able to qualitatively and quantitatively allow the identification of each of the three components of the urethane dissociation equilibrium. The technique should also be applicable over a range of temperatures and a range of physical states. Spectroscopic techniques that were considered included solid state NMR analysis, NMR analysis in the molten state but not in solution, ultraviolet spectroscopy and infrared spectroscopy. For the characterization of the urethanes included in this study, hot-stage infrared spectroscopy was chosen as the most useful technique.

The thermally reversible dissociation of the aromatic urethane bond could be directly followed using hot-stage infrared spectroscopy (HS-IR), and this

technique had several advantages. First, HS-IR spectroscopy permitted the direct observation of the appearance of the NCO stretching absorption at elevated temperatures as well as the disappearance of the urethane $C=O$ stretching absorption. Second, HS-IR spectroscopy was applicable for a variety of chemical and physical states of the urethanes such as pure solids, pure molten films, solid suspensions in an inert medium, or solutions in a non-volatile solvent. The capability of observing the infrared spectra of the pure solids at elevated temperatures was beneficial to this research since the model urethanes as well as the polyurethanes were solids. Third, infrared spectroscopy might be used to quantitatively determine the composition of mixtures.

Before characterizing the urethanes in the pure state, preliminary hot-stage infrared spectroscopic studies were done as suspensions in Nujol to determine the range of temperatures at which dissociation would begin and if the reaction could be shown to be a reversible reaction. A Nujol suspension was prepared, and the sample was smeared between two polished NaCl discs, then sealed with a thin Teflon spacer. The NaCl discs were assembled as part of a demountable variable temperature infrared cell to obtain infrared spectra as a function of temperature. As the temperature of the cell was increased, the sample was analyzed for the appearance of the isocyanate stretching absorption at approximately 2280 cm^{-1}, as well as for the disappearance of the urethane carbonyl stretching absorption in the region of 1800-1700 cm^{-1}. With increasing temperature, the strength of the isocyanate stretching absorption increased; and the strength of the urethane carbonyl stretching absorption decreased. The ratio of the intensity of the isocyanate absorption relative to the intensity of the carbonyl absorption strength was plotted as a function of temperature for N-phenyl phenyl carbamate (6), Figure 4-13. The Y axis represents the ratio of the isocyanate

Figure 4-13. Ratio of isocyanate to urethane carbonyl absorption as a function of temperature as a thin film of N-phenyl phenyl carbamate in Nujol.

absorbance to the carbonyl absorbance; a ratio of 0 indicates that no reversal has occurred. The reversal reaction itself did not begin until approximately 100°C, and that as the temperature increased, the reversal reaction increased almost linearly as a function of temperature. As the temperature was decreased, the equilibrium shifted towards formation of urethane; and as the temperature was increased, the equilibrium shifted towards formation of isocyanate and alcohol. The reaction was cycled several times proving that this experiment was useful in observing the reversible dissociation of the urethane to the isocyanate and phenol.

Figure 4-14 provides similar data for N-4-methoxyphenyl 4-nitrophenyl carbamate (<u>30</u>). A striking difference was apparent between this curve and that for N-phenyl phenyl carbamate (<u>6</u>). The relationship was still linear, but the slope
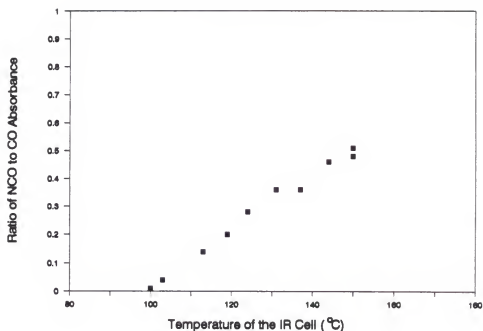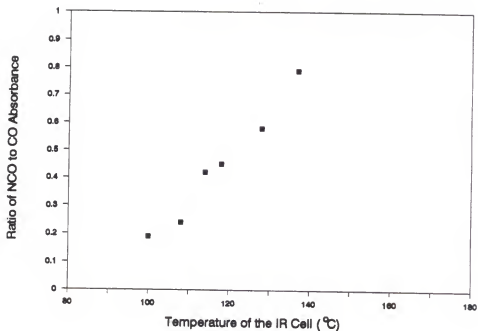
Figure 4-14. Ratio of isocyanate to urethane carbonyl absorption as a function of temperature of a thin film of N-4-methoxyphenyl-4-nitrophenyl carbamate in Nujol.

of the line was considerably greater than for N-phenyl phenyl carbamate. These HS-IR experiments showed that an electron-donating group present on the isocyanate and an electron-withdrawing group present on the phenol, increased the value of the equilibrium constant at any given temperature. As before, the reversal reaction itself did not actually begin until 100°C.

In order to imitate the situation for bulk properties, the aromatic-aromatic urethane bond was characterized in the absence of Nujol using HS-IR techniques. The urethanes in Table 4-4 were examined as bulk films by first dissolving the urethane in a dry, volatile solvent and then applying small amounts of this solution dropwise onto a polished sodium chloride disc, and the disc was placed in the

Table 4-4. First Onset of Dissociation Of Substituted Model Urethanes from HS-IR
Experiments in Bulk.

	Urethane	DSC[a] m.p. (°C)	Dissoc Temp(°C)
(6)	PhNHCO$_2$Ph	126	125
(27)	O$_2$NPhNHCO$_2$Ph	163	176
(28)	CH$_3$OPHNHCO$_2$Ph	157	141
(16)	PhNHCO$_2$PhNO$_2$	147	134
(29)	O$_2$NPhNHCO$_2$PhNO$_2$	227	---
(30)	CH$_3$OPhNHCO$_2$PhNO$_2$	134	146
(15)	PhNHCO$_2$PhOCH$_3$	136	137
(31)	O$_2$NPhNHCO$_2$PhOCH$_3$	186	---
(32)	CH$_3$OPhNHCO$_2$PhOCH$_3$	180	172

a) DSC scan rates were at 10°C/min

variable temperature infrared cell. The bulk urethane film was scanned at various temperatures from room temperature to as high as 200°C, the upper limit of the heated cell. No detectable NCO stretching absorption was observed until the pure urethane had begun to become slightly molten or completely melted, at which point the appearance of the NCO stretching absorption was clearly evident. Data for these experiments is presented in Table 4-4.

During the initial heating of the bulk urethanes, no evidence for dissociation was observed at temperatures below 100°C, compared to the Nujol studies, simply because the compounds themselves did not melt. Stated another way, the reversal reaction did not occur in the crystal itself. Once melting occurred, however, the reversal reaction began, and equilibrium was established quite rapidly. The equilibrium shifted towards formation of isocyanate and phenol at a rate dependent upon the nature of the substituent present on the aromatic ring. The data presented in Table 4-4 corroborates this hypothesis. Note that dissociation temperatures compared very closely with the melting points of these

compounds and in some cases were quite exact. These results were particularly interesting and suggested that in order for useful reversal reactions to occur, the temperature expected for reversal must be above that of the melting point of the urethane itself.

Since dissociation generally occurred very close to the measured melting point, it was not clear whether the urethane was first melting and then dissociating or whether the urethane was beginning to first dissociate to produce alcohol and isocyanate compounds which depress the melting point of the remaining undissociated urethane. If the urethane must first melt before dissociating, this suggests that the activation energy for dissociation in the pure state is greater than the heat of fusion. If the activation energy for dissociation is less than the heat of fusion, then the urethane may not necessarily melt but may more correctly be considered to decompose; thus, the observed melting point would be greater than the dissociation temperature.

These experiments also demonstrated that the dissociation was reversible. Upon cooling the dissociated sample in the sealed cell, the strength of the isocyanate stretching absorption noticeably decreased as the temperature decreased; and it was observed that an isocyanate stretching absorption was still apparent even when the temperature was cooled well below the melting point of the urethane, Figure 4-15. If the temperature of the sample was cooled and maintained at a temperature slightly below the melting point of the urethane, the isocyanate stretching absorption was still observed as long as the sample was molten. Upon cooling even further, the isocyanate stretching absorption eventually disappeared, and the disappearance of the isocyanate absorption was found to coincide with the solidification of the previously molten sample. An explanation of this is that upon recombination of the isocyanate and phenol (their
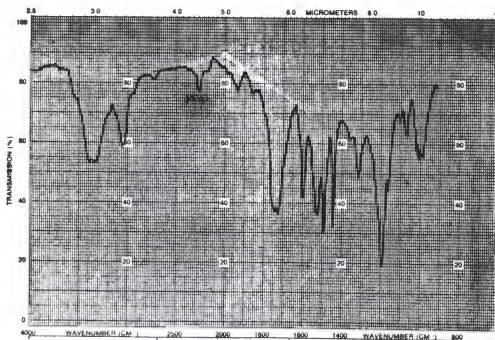
Figure 4-15. IR spectra of N-phenyl phenyl carbamate while still molten but below its melting point.

melting points being less than the corresponding urethane), the urethane would then crystallize. This process of heating and cooling could be repeated, and with each cycle the NCO stretching absorption would appear when the bulk urethane had become molten and would disappear upon cooling and solidifying.

In an effort to examine more closely the effect of physical state upon dissociation, N-phenyl phenyl carbamate (6) was also studied in solution. It had already been shown that solutions of some substituted aromatic-aromatic urethanes thermally dissociated in ethylene glycol dimethyl ether and diethylene glycol dimethyl ether. However, these solvents themselves could serve as proton transfer agents. To evaluate more clearly the effects of physical state, it was

necessary to examine the thermal dissociation in a solvent that would not be involved in the equilibrium dissociation mechanism. An appropriate solvent is o-dichlorobenzene. Dissociation occurred at a lower temperature than in the bulk state.

When the crystal structure of the urethane is destroyed using a non-solubilizing solvent, it dissociates at a lower temperature. Apparently the activation energy for dissociation of the urethane bond itself is lower than the activation energy of the urethane bond observed in the pure crystalline state. Thus the physical state of a urethane compound must be considered when determining the physical properties of an aromatic-aromatic urethane compound.

Attempt to Use HS-IR to Quantitatively Measure the Reversibility of the Model Urethanes

As stated previously, infrared spectroscopy can be a useful tool for quantitatively determining the composition of mixtures, particularly mixtures containing strongly absorbing and very distinguishable functional groups such as the NCO and urethane $C = O$ groups.[68-73] The Beer-Lambert relationship can be used to correlate the intensity of an absorption band at a specific wavelength to the concentration of the functional group absorbing the radiation. In a dilute solution, Beer's law describes the relationship between absorbance and concentration and is expressed as

$$A_x = a_x * b_x * c \qquad \text{Equation 4-1}$$

where A is the absorbance intensity in the infrared spectrum at wavelength x; a is the molar absorptivity coefficient; b is the cell path length; and c is the molar concentration of absorbing species. The thermally reversible dissociation of

Figure 4-16. Dissociation equilibrium for aromatic urethane.

urethanes can be considered an equilibrium reaction as written in Figure 4-16. The equilibrium is described by the constant, K, relative to the concentrations of the participating species. In the present case,

$$K = \frac{[\,NCO\,]\,[\,OH\,]}{[\,URETHANE\,]} \qquad \text{Equation 4-2}$$

where K is the equilibrium constant and [ ] denotes the molar concentration of the enclosed species. Since the equilibrium of the urethane dissociation is a function of temperature, an expression relating the effect of temperature on the constant, K, can be derived from the Gibbs free energy, ΔG

$$\Delta G = -RT \ln K \qquad \text{Equation 4-3}$$

and

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation 4-4}$$

where R is the gas constant; T is the absolute temperature; ΔH is the enthalpy and ΔS is the change in entropy. Therefore, combining equation 4-3 and 4-4 and solving for lnK yields

$$\ln K = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \qquad \text{Equation 4-5}$$

Equation 4-5 shows that a linear relationship can exist between lnK and 1/T, and a plot of lnK versus 1/T gives a straight line with a slope of $-\Delta H/R$ and an intercept of $\Delta S/R$[70]. Now substituting equation 4-2 gives

$$\ln \frac{[NCO][OH]}{[URETHANE]} = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \qquad \text{Equation 4-6}$$

From this equation, it is possible to see how temperature affects the extent of the dissociation of the urethane bond and the concentrations of each of the components. As the temperature is increased the concentration of NCO will increase, and the concentration of urethane will decrease. By determining the concentration of NCO and urethane present as a function of temperature, the ΔH and ΔS for the thermally reversible dissociation of the urethane bond could be determined.

Qualitatively, it was shown that dissociation occurred reversibly in several solvents and in the bulk state. It was attempted to quantitatively determine the extent of reversible dissociation using HS-IR spectroscopy of thin deposited films of the urethanes. These films were deposited from dry, volatile solvents such as chloroform and acetone; and the infrared spectra were then collected at selected temperatures that ranged from below the melting point of the urethane to below the boiling point of the most volatile compound involved in the reversible dissociation equilibrium. In each of these spectra, the intensity of several absorption bands was measured at various temperatures.

Experimentally, this technique was not trivial, especially when working with thin films of the urethane sample in bulk. Several attempts were made to devise

procedures to assure that the concentration of liquid urethane and its reaction components would maintain a constant total concentration during the experiment itself with no loss of material due to a leak or vaporization of any material.

In an attempt to correlate the change in concentration of isocyanate as a function of temperature, a peak ratio method was used. This method involved determining the absorption intensity of the isocyanate stretch as well as the intensity of an absorption band that would not change relative to a change in the extent of dissociation. The ratio of the absorbances for these two bands were plotted as a function of temperature. Some examples of these curves are given in Figures 4-17 and 4-18. These curves support the conclusion that dissociation is increasing as a function of temperature, but it was not possible to quantitatively
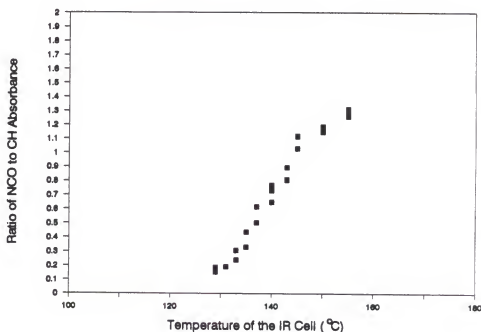

Figure 4-17. Ratio of isocyanate absorbance to C-H absorbance as a function of temperature for N-phenyl phenyl carbamate in the bulk state.
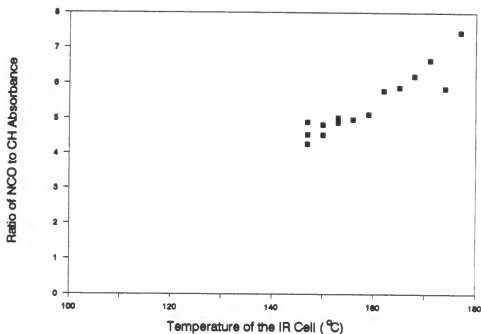
Figure 4-18. Ratio of isocyanate absorbance to C-H absorbance as a function of temperature for N-4-methoxyphenyl 4-nitrophenyl carbamate in the bulk state.

determine the thermodynamic parameters for the reversible dissociation

equilibrium. An example of how the dissociation proceeded as the temperature

was increased can be seen in Figure 4-19.

The carbonyl region of the infrared spectrum was also observed at the

various temperatures. The change in the strength of the carbonyl absorption was

difficult to determine. As the temperature of the sample was increased the shape

of the carbonyl absorption changed. As a deposited film at lower temperatures,

the carbonyl absorption was observed as a strong, sharp absorption. In some

cases as the temperature of the sample was increased, the carbonyl absorption

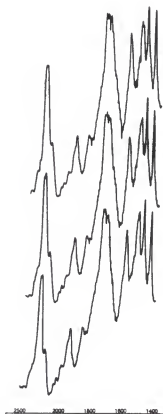became considerably broader and no longer exhibited a sharp absorption

Figure 4-19. Variable temperature IR spectra of N-phenyl phenyl carbamate in the bulk state: top) 150°C, middle) 140°C, and bottom) 135°C.

maxima. In some cases as the temperature was increased, a second absorption was observed as a shoulder peak at higher wavenumbers that gradually increased in intensity while the original carbonyl absorption appeared to decrease. In other cases as the temperature was increased the position of the absorption maxima shifted to a higher wavenumber in addition to becoming broader in appearance. These changes in absorption band shape caused difficulties in correlating the disappearance of carbonyl stretching absorption as a function of temperature.

The attempts to experimentally determine quantitatively the extent of dissociation in the bulk state using HS-IR were unsuccessful in yielding values for

ΔH, ΔG, ΔS and K, but the apparent change in concentration of isocyanate did show that dissociation would increase as the temperature was raised. The changes in physical state during dissociation of the urethanes prohibited the quantitative determination of the dissociation equilibrium. The reversible dissociation could not be quantitatively determined due to problems concerning the homogeneous dispersion of the material, and the amount of light passing through void space could not be adequately determined. This problem could be ignored if the transformation that was being analyzed occurred in the solid state because the amount of void space would remain relatively constant at the various temperatures. The problem could also be eliminated if the dissociation occurred after the sample had completely finished melting. Similarly, if the sample was liquid before and after the dissociation occurred a thin film could be prepared which could eliminate void space. It was also difficult to prepare a bulk film thin enough to prevent the more strongly absorbing urethane carbonyl absorption from being off scale. These problems caused deviations in the relationship between peak intensity and concentration and were discussed by Jones[71] as problems encountered in quantitative IR analysis, and these prevented the use of HS-IR for quantitative analysis in our study.

CHAPTER 5
THERMAL CHARACTERIZATION OF PREPOLYMERS AND POLYMER

The thermal properties of the urethane bond as part of a polymer are described in this chapter. The methods discussed previously for the characterization of the model urethanes in chapter 4 were used to characterize the thermal properties of the prepolymers, (41) and (43), and the poly(oxyethylene-urethane), (44). In the model compound studies, it was observed that substituents and physical state of a urethane compound affected the thermal properties of the urethane bond, and this would suggest that the thermal properties of the urethane bond in a polymer could be greatly different from those observed for a similar model compound. Since the physical state was shown to be related to the ability of the urethane bond to dissociate, it was envisioned that in an appropriate polyurethane dissociation could be observed at lower temperatures than for a structurally similar model urethane. The premise was that in a polyoxyethylene chain extended via a urethane bond the polymer would melt at an appreciably lower temperature than an electronically similar model urethane and permit a better determination of the temperature of dissociation. At this point, the poly(oxyethylene-urethane) (44) and the two precursor prepolymers, (41) and (43), Figure 5-1, were characterized. The synthetic route to the two prepolymers has been discussed previously.

HO-⬡-(OCH₂CH₂)₃O-⬡-OH   H₂N-⬡-(OCH₂CH₂)₃O-⬡-NH₂

(41)   (43)

Figure 5-1. Structure of the prepolymers.

DSC and TGA Analyses of Prepolymers and Polymer

The prepolymers were characterized using DSC and TGA. Only melting endothermic transitions were observed for the bis-phenol (43) and bis-amine (41) in the DSC analyses. No other thermal transitions were observed to indicate any decomposition processes occurring over the range of temperatures chosen. This observation was also supported by TGA analyses which showed only single weight loss transitions occurring indicative of the vaporization of the prepolymers; the onset of weight loss was above 225°C for both prepolymers (41) and (43), and only a residual amount of material remained. Therefore, the prepolymers are considered thermally stable over the range of temperatures chosen.

Before analyzing the poly(oxyethylene-urethane) (44), two model prepolymeric urethanes were studied. These two prepolymer urethanes, (54) and (55), were synthesized by endcapping the 1,2-bis(2-(4-aminophenoxy)ethoxy)-ethane with urethane groups, Figure 5-2. The samples were heated at a rate of 10°C/min in the DSC. In the phenol blocked case (54), a melting endotherm was observed at 154°C followed by a very broad endotherm from 206-241°C; this latter endotherm was due to vaporization of phenol. In comparison with the similar model urethane, N-4-methoyxphenyl phenyl carbamate (30), the melting point was 157°C. The DSC of the ethoxyphenol case (55) showed a small endotherm bump at 141°C followed by a melting endotherm at 206°C. A small
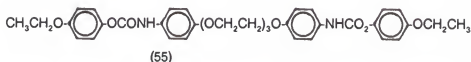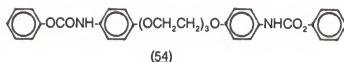
(54)

(55)

Figure 5-2. Urethane endcapped 1,2-bis(2-(4-aminophenoxy)ethoxy)ethane.

endotherm was observed later at 233°C due to the vaporization of the ethoxyphenol. Again as a comparison, the similar model urethane, N-4-methoxyphenyl 4-methoxyphenyl carbamate (32), had a melting point of 187°C.

Table 5-1. DSC Data for the Endcapped Urethanes.

	R	T_m (°C)	ΔH (J/g)	Heating Rate (°C/min)
(54)	H	154	124	10
(55)	CH_3CH_2O	206	99	10

In the of the phenol blocked prepolymer (54), dissociation occurred according to the reaction of Figure 5-3 in which two molecules of phenol would be produced that would vaporize since the boiling point of phenol, 182°C, is lower than that of 1,2-bis(2-(4-isocyanatophenoxy)ethoxy)ethane (42). The loss of two molecules of phenol results in a theoretical weight loss of 33%. In the TGA
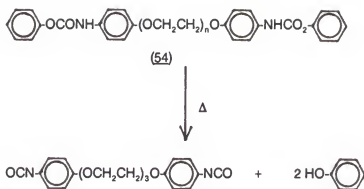
Figure 5-3. Dissociation scheme for phenol blocked 1,2-bis(2-(4-isocyanatophenoxy)ethoxy)ethane.

experiments, multiple weight loss transitions were observed; and the TGA analyses showed that dissociation was occurring and that the phenol products were vaporizing. When bis(1,2-bis(phenoxyethoxy)ethyl phenyl carbamate (54) was heated at 10°C/min, three transitions were observed, Figure 5-4. The first transition was a loss of 33% from 179-244°C produced by the vaporization of phenol. A second transition of a loss of 47% occurred from 244-306°C due to vaporization of the bis-isocyanate (42). The last transition of 18% resulted from continued vaporization of (42) as well as other decomposition reactions leaving a charred residue accounting for 3.3%.

Likewise, in the thermal dissociation of the 4-ethoxyphenol blocked case (55), there was the loss of 2 molecules of 4-ethoxyphenol. The theoretical weight loss for 2 ethoxyphenol groups would produce a weight loss of 42%. When bis(1,2-bis(phenoxyethoxy)ethyl 4-ethoxyphenyl carbamate (55) was heated at 10°C/min, three transitions were observed, Figure 5-5. The first transition was a loss of 40% due to vaporization of 4-ethoxyphenol (boiling point of 246°C). A second transition of a loss of 24% occurred over the same temperature range,
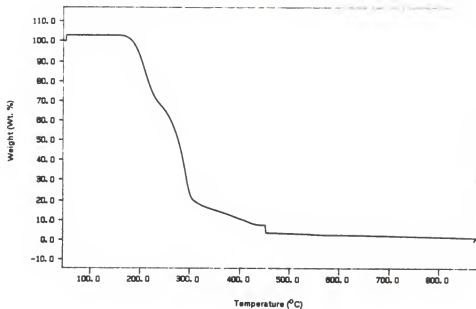
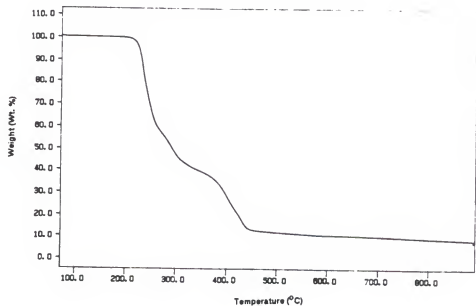Figure 5-4. TGA curve of bis(1,2-bis(phenoxyethoxy)ethyl) phenyl carbamate (49) at 10°C/min.

Figure 5-5. TGA curve of bis(1,2-bis(phenoxyethoxy)ethyl) 4-ethoxyphenyl carbamate (50) at 10°C/min.

260-310°C, as the phenol blocked case (54) accounting for the vaporization of some of the bis-isocyanate (42).

The poly(oxyethylene-urethane) (44) was studied using DSC. The DSC of a sample of the polymer product (44) showed no endotherms nor exotherms when heated as high as 600°C. A similar pattern had previously been observed for other polyurethanes studied by Kinstle and Sepulveda.[33] This would suggest that the polyurethane (44) is dissociating to a large extent without melting. A TGA analysis at 10°C/min showed two transitions, Figure 5-6. The first transition was a loss of 61% from 233-340°C and was within the temperature range observed for the weight loss of the bis-phenol (43), bis-amine (41), and bis-isocyanate (42). The final weight loss of 35% occurred between 340-900°C leaving 4% of a charred residue.
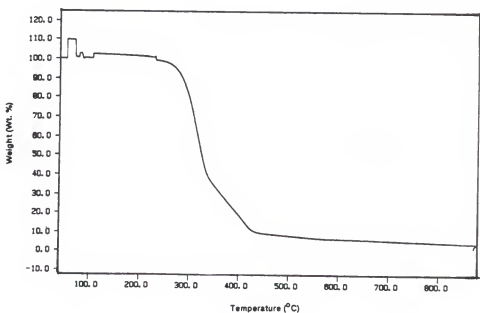

Figure 5-6. TGA curve of the poly(oxyethlyene-urethane) (39) at 10°C/min.

These experiments demonstrated that dissociation was occurring in the prepolymeric and polymeric urethanes and that the temperatures were still abouve the melting point of the materials.

Hot-Stage Infrared Spectroscopy of Prepolymers and Polymer

As in the case of the small model aromatic urethanes, no direct evidence of the dissociation equilibrium could be ascertained from DSC and TGA methods. Hot-stage infrared spectroscopy was used in an attempt to provide direct evaluation of the dissociation equilibrium of the prepolymeric and polymeric urethane. In the HS-IR studies of the model urethanes, the absorbance of the functional groups in the pure films generally were too strong, particularly the urethane carbonyl. It was envisioned that in a polyurethane the intensity of absorptions would be decreased.

In a poly(oxyethylene-urethane) (44), the effective molar concentration of $C=O$ group could be decreased by increasing the length of the chain extended polyether, and the effective relative molar concentration of $C=O$ in the polyether urethane would decrease. This effect would be evident as a greatly decreased molar extinction coefficient. A smaller molar extinction coefficient would allow the change in the strength of the absorption of the urethane carbonyl to be observed as a function of temperature and therby as a function of reversible dissociation.

Additionally, the change of the relative molar concentration of carbonyl relative to the molecular weight of the polymer should also effect the equilibrium nature of the reversible dissociation. In general, when describing an equilibrium system, pure liquids and solids are not incorporated into the equilibrium expression since the concentration of a pure liquid or solid does not change. However, in a system where the portion of the molecule involved in the equilibrium

contributes only a portion of the mass of the molecule the concentration of the pure substance must be incorporated into the equilbrium expression. As the size of the urethane compound increases, the actual concentration of urethane functional group is effectively reduced. Therefore, although the urethane compound itself is a pure substance, the urethane functional group can be treated as if the urethane bond is not a pure substance. In the poly(oxyethylene-urethane) system (44), the equilibrium system can be treated as the thermally reversible dissociation of "ideal" model urethane (52) in polyoxyethylene. The analysis of N-4-methoxyphenyl 4-methoxyphenyl carbamate (32) in diethylene glycol dimethyl ether could also be treated as a model for the polymer systems. However, this comparison can only be extended to a poly(oxyethylene-urethane) in which the polyether segments are long such that the polymer itself actually resembles a solution of an aromatic-aromatic urethane in polyoxyethylene. This comparison could not be extended to the polyether urethanes containing short segments of ethylene oxide.

HS-IR spectroscopy was used to examine the dissociation properties of the urethane blocked prepolymers, (54) and (55), and the poly(oxyethylene-urethane) (44). As was shown in the model urethane series, dissociation was prohibited below the melting point of the respective urethane compounds. The first evidence of dissociation of the phenol blocked prepolymer (54) was observed upon melting although it was not possible to evaluate the full dissociation properties due to the high melting point of this material.

The HS-IR studies could not be performed upon the 4-ethoxyphenol blocked prepolymer (55) nor the poly(oxyethylene-urethane) (44) since these urethane samples exhibited such high melting points that they could not be melted in the hot-stage infrared cell; the temperature limit of the temperature
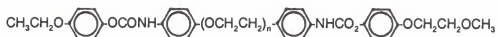
controller was 200°C. As previously shown, dissociation of these types of urethanes were linked to the melting point. As in the model studies, no dissociation was observed during the heating of the sample to temperatures below the melting point. This supports the conclusion that in some cases dissociation is dependent upon the physical state. In the following series
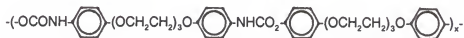
$$CH_3O-\langle\bigcirc\rangle-NHCO_2-\langle\bigcirc\rangle-OCH_3$$

$$T_m = 187°C \qquad \Delta H = 119 J/g$$

$$CH_3OCH_2CH_2O-\langle\bigcirc\rangle-NHCO_2-\langle\bigcirc\rangle-OCH_2CH_2OCH_3$$

$$T_m = 155°C \qquad \Delta H = 125 J/g$$

$$CH_3CH_2O-\langle\bigcirc\rangle-OCONH-\langle\bigcirc\rangle-(OCH_2CH_2)_n-\langle\bigcirc\rangle-NHCO_2-\langle\bigcirc\rangle-OCH_2CH_2OCH_3$$

$$T_m = 206°C \qquad \Delta H = 103 J/g$$

$$-(-OCONH-\langle\bigcirc\rangle-(OCH_2CH_2)_3O-\langle\bigcirc\rangle-NHCO_2-\langle\bigcirc\rangle-(OCH_2CH_2)_3O-\langle\bigcirc\rangle-)_x-$$

Does not melt

the four compounds have similar types of urethane bonds; therefore, dissociation should occur at comparable temperatures since the activation energy for dissociation of each of these substances should be very close. However, since

the melting points of these compounds differed, the temperature at which dissociation occurred were different suggesting that the activation energy was greater than their heats of fusion, ΔH_f. In some cases the trend may be quite the opposite as observed when comparing the following two urethanes
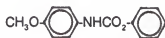
$T_m = 157°C$ $\qquad$ $\Delta H = 144 J/g$
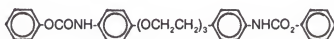
$T_m = 154°C$ $\qquad$ $\Delta H = 124 J/g$

This would explain why no melting endotherm was observed for the poly(oxyethylene-urethane) (44). It was slowly dissociating without truly melting. Since most polyurethanes are in fact amorphous, they may not exhibit a clear melting point but may exhibit a softeneing point.

<div align="center">Conclusions</div>

In this research, the synthesis of various model, prepolymeric and polymeric urethanes had been accomplished. These compounds were specifically designed to permit the characterization of the thermally reversible properties of the aromatic-aromatic urethane bond without the interferences from other thermally labile bonds. The studies using DSC, TGA and HS-IR provided useful information into the dissociation of urethanes in the bulk state. The DSC and TGA experiments demonstrated that dissociation in bulk was still an

equilibrium reaction with no apparent non-reversible side reactions for the aromatic-aromatic type of bond. HS-IR provided direct evidence of the formation of isocyanate during heating, and the amount of isocyanate increased with temperature. The HS-IR studies demonstrated that the reaction was reversible in that the isocyanate was no longer observed upon cooling; and that upon reheating the sample, the presence of isocyanate was again observed.

The characterization studies also demonstrated that the physical state of the urethane was an important factor in its ability to dissociate. Urethanes that were previously shown in this work and by others to dissociate in solvents below 100°C did not begin to dissociate in bulk until the material had melted. These temperatures were higher than 100°C.

Therefore, it becomes evident that the thermally reversible properties of urethanes are dependent upon the structure and physical state of the compound.

REFERENCES

1. A. Wurtz, _Ann._, _71_, 326 (1849).

2. A. W. Hofmann, _Ann._, _74_, 9 (1850).

3. J. H. Saunders and K. C. Frisch, "Polyurethanes: Chemistry and Technology, Part I: Chemistry," Interscience Publishers, New York, 1962.

4. J. H. Saunders and K. C. Frisch, "Polyurethanes: Chemistry and Technology, Part II: Technology," Interscience Publishers, New York, 1964.

5. D. J. David and H. B. Staley, "Analytical Chemistry of the Polyurethanes," Interscience Publishers, New York, 1969.

6. G. Oertel, "Polyurethane Handbook," Carl Hanser Verlag, Munich, 1985.

7. R. Leuckart, _J. prakt. Chem._, _41_, 318 (1890).

8. T. Hoshino, T. Mukaiyama and H. Hoshino, _Bull. Chem. Soc. Jpn._, _25_, 396 (1952).

9. T. Mukaiyama and Y. Hoshino, _J. Amer. Chem. Soc._, _78_, 1946 (1956).

10. T. Mukaiyama and M. Iwanami, _J. Amer. Chem. Soc._, _79_, 73 (1957).

11. T. Mukaiyama, T. Akiba and T. Asahi, _Bull. Chem. Soc. Jpn._, _33_, 1137 (1960).

12. T. Mukaiyama and T. Akiba, _Bull. Chem. Sco. Jpn._, _33_, 1707 (1960).

13. N. G. Gaylord, _J. Org. Chem._, _25_, 1874 (1960).

14. T. Hoshino, T. Mukaiyama and H. Hoshino, _J. Amer. Chem. Soc._, _74_, 3097 (1952).

15. T. Hoshino, T. Mukaiyama and H. Hoshino, _Bull. Chem. Soc. Jpn._, _25_, 392 (1952).

16. T. Hoshino, T. Mukaiyama and H. Hoshino, _Bull. Chem. Soc. Jpn._, _25_, 396 (1952).

17. T. Mukaiyama and T. Matsunaga, _J. Amer. Chem. Soc._, _75_, 6209 (1953).

18. H. W. Blohm and E. I. Becker, _Chem. Revs._, _51_, 471 (1952).

19. N. M. Bortnick, L. S. Luskin, M. D. Hurwitz and Q. W. Rytina, J. Amer. Chem. Soc., 78, 4358 (1956).

20. E. Dyer, G. E. Newborn and G. C. Wright, "Thermal Degradation of Carbamates," Delaware Chemical Symposium, February 1958.

21. E. Dyer and G. E. Newborn, J. Amer. Chem. Soc., 80, 5495 (1958).

22. E. Dyer and G. Wright, J. Amer. Chem. Soc., 81, 2138 (1959).

23. H. Lakra and F. B. Dains, J. Amer. Chem. Soc., 51, 2220 (1929).

24. C. B. Reilly and M. Orchin, "The Dissociation of Ureas, Urethanes and Biurets," Symposium on Isocyanate Polymers, American Chemical Society Meeting (1956).

25. J. Swerdloff and S. B. McFarlane, "Thermal Degradation of Polyurethanes," American Chemical Society Meeting, September 1954.

26. A. B. Lateef, J. A. Reeder and L. Rand, J. Org. Chem., 36, 2295 (1971).

27. W. E. Catlin, US Pat 2284637 (to DuPont) June 2, 1942.

28. O. Bayer, Angewandte Chemie, A59, 275 (1947).

29. O Bayer, E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth, Angewandte Chemie, 62, 57 (1959).

30. O Bayer, E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth, Rubber Chemistry and Technology, 23, 812 (1950).

31. A. Hochtlen, Kunststoffe, 42, 303 (1952).

32. O. Bayer, H. Rinke, W. Siefken, L. Orthmer and H. Schild, Ger. Pat. 728,981 (to I. G. Farbenindustrie), Nov. 12, 1942.

33. J. F. Kinstle and L. E. Sepulveda, Polymer Letters Ed., 15, 467 (1977).

34. A. Orzeszko and A. Kolbrecki, J. Appl. Poly. Sci., 25, 2969 (1980).

35. M. P. Thorne, Can. J. Chem., 45, 2537 (1967).

36. E. Dyer and R. E. Reed, J. Org. Chem., 26, 4388 (1961).

37. J. R. Saunders, Rubber Chem. Technol., 32, 337 (1959).

38. R. Simha, D. J. Ingham, N. S. Rapp and J. Hardy, J. Poly. Sci. B, 2, 675 (1964).

39. N. S. Rapp and D. J. Ingham, J. Poly. Sci. A, 2, 689 (1964).

40. D. J. Ingham and N. S. Rapp, J. Poly. Sci. A, 2, 4941 (1964).

41. L. P. Rumao and K. C. Frisch, J. Poly. Sci. A-1, 10, 1499 (1972).

42. H. H. G. Jellinek and K. Takada, J. Poly. Sci.: Poly. Chem. Ed., 13, 2709 (1975).

43. M. L. Matusak and K. C. Frisch, J. Poly. Sci.: Poly. Chem. Ed., 11, 637 (1973).

44. N. Grassie and M. Zulfigar, J. Poly. Sci.: Poly. Chem. Ed., 16, 1563 (1978).

45. K. J. Voorhees, F. D. Hileman, I. N. Einhorn and J. H. Futrell, J. Poly. Sci.: Poly. Chem. Ed., 16, 213 (1978).

46. A. Ballistreri, S. Foti, P. Maravigna, G. Montaudo and E. Scamporrino, J. Poly. Sci. Poly. Chem. Ed., 18, 1923 (1980).

47. A. Ballistreri, S. Foti, P. Maravigna, G. Montaudo and E. Scamporrino, J. Appl. Poly. Sci., 26, 2781 (1981).

48. R. Bill, M. Droscher and G. Wegener, Makromol. Chem., 182, 1033 (1981).

49. Y. Kawakami, R. A. N. Murthy and Y. Yamashita, Polymer J., 13, 343 (1981).

50. M. M. Coleman, K. H. Lee, D. J. Skrovanek and P. C. Painter, Macromolecules, 19, 2149 (1986).

51. H. S. Lee, Y. K. Wang and S. L. Hsu, Macromolecules, 20, 2089 (1987).

52. A. J. Gordon and R. A. Ford, "The Chemist's Companion: A Handbook of Practical Data, Techniques and References," 4th ed., John Wiley and Sons, New York, 1972.

53. R. A. W. Johnstone and M. E. Rose, Tetrahedron, 35, 2169 (1979).

54. J. G. Hoggett, R. B. Moodie, J. R. Penton and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge University Press, Cambridge, 1971.

55. S. Ram and R. E. Ehrenkaufer, Tetrahedron Letters, 25, 3415 (1984).

56. Z. Jedlinski, J. Franek and P. Kuziw, Makromol. Chem., 187, 2317 (1986).

57. T. Cohen, A. Dietz Jr. and J. Miser, J. Org. Chem., 42, 2053 (1977).

58. K. Fuji, K. Ichikawa, M. Node and E. Fujita, J. Org. Chem., 44, 1661 (1979).

59. K. Kurita and Y. Iwakura, Org. Synthesis, 59, 195 (1979).

60. B. S. Furniss, A. J. Hannaford, P. W. G. Simth and A. R. Tatchell, "Vogel's Textbook of Practical Organic Chemistry," 5th ed., Longman Scientific and Technical, London, 1989.

61. W. Feld, B. Ramalingam and F. Harris, J. Poly. Sci.: Poly. Chem. Ed., 21, 319 (1983).

62. S. Hazlet and C. Dornfeld, J. Amer. Chem. Soc., 66, 1781 (1944)

63. T. Neilson, H. C. S. Wood and A. G. Wylie, J. Chem. Soc. pt. I, 371 (1962).

64. B. S. Furniss, A. J. Hannaford, P. W. G. Simth and A. R. Tatchell, "Vogel's Textbook of Practical Organic Chemistry," 5th ed., Longman Scientific and Technical, London, 1989.

65. R. J. Slocombe, E. E. Hardy, J. H. Saunders and R. L. Jenkins, J. Amer. Chem. Soc., 72, 1888 (1950).

66. E. A. Turi, "Thermal Characterization of Polymeric Materials," Academic Press, New York, 1981.

67. J. H. Flynn, "Polymers: Polymer Characterization and Analysis," J. I. Kroschwitz, ed., John Wiley and Sons, New York, 1990.

68. M. M. Coleman and P. C. Painter, "Polymers: Polymer Characterization and Analysis," J. I. Kroschwitz, ed., John Wiley and Sons, New York, 1990.

69. W. J. Potts, Jr., "Chemical Infrared Spectroscopy, vol I, Techniques," John Wiley and Sons, New York, 1963.

70. W. O. George and J. E. Goodfield, "Analytical Applications of FT-IR to Molecular and Biological Systems," J. R. Durig, ed., D. Reidel Publishing Company, Amsterdam, p. 299, 1980.

71. R. N. Jones, J. Amer. Chem. Soc., 74, 2681 (1952).

72. J. L. Koenig, Anal. Chem., 36, 1045 (1964).

73. C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, 1963.

BIOGRAPHICAL SKETCH

Mark Allen Murla was born on December 5, 1962, in Pensacola, Florida, under the sign of Sagitarrius (The Hunter); and so the hunt began. Growing up in New Orleans and Pensacola, he learned to appreciate the southern way of life.
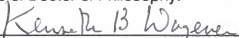
After graduating from the University of West Florida in 1984, Mark began his graduate studies at the University of Florida under the guidance of Dr. Ken Wagener. From that time forward, Mark would forever bleed Gator Orange and Blue.

During this time, Mark was exposed to the ways of the world. Thanks to Dr. Wagener, Mark spent the summer of 1988 living and doing research in Freiburg, West Germany (before democracy re-emerged in Eastern Europe). It was hard to concentrate on research while surrounded by the beauty and splendor of the Black Forest. During this time, Mark learned a great deal about the world and gained a new perspective of the United States.
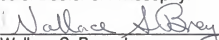
Shortly after returning to the US, Mark completed his research and began an industrial career with BASF Corporation in Asheville, NC. While juggling the responsibilities of corporate life, he finally finished his dissertation in 1991.
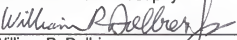
The hunt continues....

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Wagener, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Wallace S. Brey, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

J. Eric Enholm
Assistant Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Christopher D. Batich
Professor of Materials Science and Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1991

Dean, Graduate School